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(54) Title: HIGH PERFORMANCE NANOCOMPOSITES

(57) Abstract: Disclosed are novel compositions that include at least one type of layered silicate as well as methods for making same. In one aspect, the invention features silicate compositions that include at least one type of layered silicate and at least one type of organophilic agent associated with the silicate. Also provided are nanocomposites that include the silicate composition and at least one suitable polymer material. The invention has a wide spectrum of useful applications including providing manufactured articles with exceptional performance characteristics.

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## HIGH PERFORMANCE NANOCOMPOSITES

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### STATEMENT OF U.S. GOVERNMENT INTEREST

Funding for the present invention was provided in part by the Government of the United States by virtue of contract No. F33615-98-C-5029 and F33615-97-C-5098 from the U.S. Air Force. Thus, the Government of the United States has certain rights in and to the invention claimed herein.

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### CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of U.S.S.N. 60/152,515 entitled "High-Temperature Use Nanocomposites" filed on September 2, 1999, which application includes the disclosure of U.S.S.N. 09/090,864 entitled "High-Temperature Polymer/Inorganic Nanocomposites" filed on June 5, 1998. The 09/090,864 application claims the benefit of U.S.S.N. 60/048,921 filed on June 6, 1997. The present application claims further benefit from U.S.S.N. 60/139,481 entitled "Nanomaterials For Barrier Applications" filed on June 17, 1999 and U.S.S.N. 60/126,048 entitled "Polymer Alloy Nanocomposites" filed on March 23, 1999. The disclosures of the 60/152,515, 09/090,864, 60/048,921, 60/139,481, and 60/126,048 applications are each hereby incorporated by reference. The present application claims priority to the U.S.S.N. 60/048,921 application filed on June 6, 1997.

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#### 1. Field of the Invention

The present invention features novel compositions that include at least one type of layered silicate. In one aspect, the invention features silicate compositions that include at least one type of layered silicate and at least one type of organophilic agent associated with the silicate. Also provided are nanocomposites that include the silicate composition and at least one suitable polymer material. The invention also features methods for making and using the silicate compositions. The present invention has a wide spectrum of useful applications including providing manufactured articles with exceptional performance characteristics.

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#### 2. Background

A nanocomposite can be defined as an interacting mixture of two phases, one of which is in the nanometer size range in at least one dimension. The precise length scale of interest in any given case is one that creates unique material properties due to the nanoscale dimensions. Nanocomposite materials offer a wealth of unique properties and technological opportunities. Hence significant research effort has been devoted to exploring their potential for a wide variety of electrical, mechanical, optical, magnetic and other applications.

Polymer/inorganic nanocomposites have attracted much attention as the properties of polymers are further enhanced beyond what is achievable from more conventional particulate-filled or micro-composites. Specifically, layered mica-type-silicates have been widely used as inorganic reinforcements for polymer matrices to create polymer nanocomposites with nanoscale dispersion of the inorganic phase within the polymer matrix. Layered silicate-polymer nanocomposites having (i) polymer chains intercalated between the silicate layers or (ii) individual silicate layers delaminated and dispersed in a continuous polymer matrix, have been fabricated.

Surface modification in the existing nanocomposites is often achieved by using an organic surfactant such as alkyl ammonium. The organic cation exchange at the oxide surface provides favorable sites for interaction between the organic and inorganic functionalities. That approach has been exploited and has been shown to offer significant performance advantages for a variety of commodity polymers. However, the thermal instability of the surfactants used has hindered that technology from realizing its full potential.

However, there has been recognition that prior silicate compositions and particularly nanocomposites have shortcomings. For example, it is increasingly apparent that many prior nanocomposites do not have the performance characteristics needed for optimal use. In particular, widespread nanocomposite use has been limited by unacceptable thermal stability, mechanical strength, interfacial design, heat distortion temperature, and polymer compatibility.

An especially significant limitation of prior silicate compositions is unacceptable use-temperature. For example, there has been understanding that use of the prior nanocomposites has been limited to commodity polymers that have been reported to have long-term use temperatures below about 150°C. Similarly, optimal use of these silicate compositions has been restricted to below that temperature.

It would be desirable to have novel silicate compositions with improved performance characteristics and particularly better long-term use above about 150°C. It would also be especially desirable to use the silicate compositions to enhance use of a wide variety of manufactured articles including those relating to the automotive, aerospace, electronic, pharmaceutical, apparel, food and beverage packaging industries.

#### **SUMMARY OF THE INVENTION**

The invention features compositions that include at least one type of inorganic layered silicate and at least one type of organophilic agent. In one aspect, the invention provides silicate compositions that include the inorganic layered silicate associated with the organophilic agent to achieve at least one desired characteristic. In another aspect, the invention provides nanocomposites that include at least one of the silicate compositions and at least one suitable polymer material. Also provided are methods for making and using the silicate compositions. The invention has many highly useful applications including providing manufactured articles with exceptional barrier properties.

We have discovered silicate compositions that feature a wide spectrum of important uses and advantages. In general, the silicate compositions represent a new generation of layered silicate compounds that provide highly desirable performance characteristics. Particular silicate compositions include at least one inorganic layered silicate associated with at least one organophilic agent to achieve the characteristics. More particular silicate compositions surprisingly provide for long-term use above about 150°C and are compatible with a wide range of polymer materials. Accordingly, the compositions and methods of this invention embody a significant advance in the

design of stable silicate compositions for long-term or short-term use at high temperature.

By the term "polymer material" or related term is meant a polymer or  
5 polymer-like material that is useful at a high temperature e.g., above about 150°C. Suitable polymer materials for use in this invention include commodity polymers, graft polymers, resins, copolymers, block polymers; as well as blends or alloys thereof. Additionally, suitable polymer materials are those that can be adapted to provide high temperature use in excess of about 200°C, preferably between from  
10 about 200°C to 450°C, with between from about 250°C to about 400°C being preferred for many applications. In embodiments in which the term "polymer material" is used to describe particular components of a nanocomposite with favorable barrier characteristics, the polymer material may also be useful at temperatures below about 150°C.

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Additionally preferred polymer materials for use in this invention are compatible with a wide variety of silicon-based layered materials and especially clay minerals such as those described below. Also preferred are polymer materials that provide good dispersion with most clay minerals while minimizing undesired  
20 plasticization.

It has also been found that many silicate compositions of this invention can be made by methods that generally enhance thermally stable surface chemistries. That is, we have learned that by associating the inorganic layered silicate with the  
25 organophilic agent, it is possible to make silicate compositions with surprising and highly desirable performance characteristics. Without wishing to be bound to theory, it is believed that the association facilitates use at high temperature. Preferred association facilitates favorable interlayer spacing within the silicate and provides for good compatibility between the silicate layers and the polymer material. Additionally  
30 preferred association helps to optimize synthetic routes and improves overall performance characteristics of the resulting end product. As an illustration, it has been found that many silicate compositions of this invention exhibit excellent

nanoscale dispersion of the inorganic layers in many commodity and high-performance polymer resins.

It has also been found that preferred nanocompositions of this invention exhibit performance characteristics that will positively impact many applications. For example, many of the nanocomposites disclosed herein offer very favorable melting and heat distortion temperatures. These and other important characteristics discussed below help make the nanocomposites and other exemplified silicate compositions well-suited for long-term or short-term use above about 150°C. As will be discussed below, many particularly preferred nanocomposites provide for even higher thermal stability in excess of about 200°C with about 250°C to about 400°C or more being useful for many applications.

It will be understood that the enhanced use temperature provided by many preferred nanocomposites of this invention can be determined by one or a combination of strategies including heat distortion tests referenced below.

Accordingly, in one aspect, the invention provides an inorganic layered silicate that includes at least one organophilic agent associated with the silicate. A preferred organophilic agent is a high temperature organic surfactant. In one embodiment, the surfactant comprises at least one onium salt, preferably at least one ammonium, phosphonium or sulfonium salt, which onium salt is non-covalently bonded to the silicate. Preferred non-covalent bonding is through one or more ionic bonds between the onium salt and the inorganic layered silicate. Also contemplated are acceptable salts of the inorganic layered silicate.

In a particular embodiment, the onium salt is present in a molar amount that is preferably less than the molar amount of exchangeable silicate ions in the composition. That is, the milliequivalent amount of the onium salt in the silicate composition is preferably less than the milliequivalent amount of exchangeable ions in the silicate. In a more particular embodiment, the onium salt is at least one of a

suitable ammonium salt, preferably an alkyl ammonium salt; or at least one of a phosphonium or sulfonium salt.

In embodiments of the invention in which the silicate composition includes at least one inorganic layered silicate and at least one of the foregoing onium salts non-covalently bond thereto, the association between the silicate and surfactant can be achieved by one or a combination of strategies including use of standard ion exchange methods. Particular use of the methods involves contacting the inorganic layered silicate and the surfactant under suitable ion exchange conditions that facilitate non-covalent binding between the onium salt and the silicate. Optionally, the ion exchange methods can be used to estimate or quantify the molar amount of ions exchanged.

If desired, particular silicate compositions in accord with this invention can be referred to the molar amount or milliequivalent of the ions exchanged.

For example, in one embodiment, the ratio of the molar amount of the onium salt to the molar amount of the exchangeable ions in the silicate is at least about 0.1 to at least about 10, preferably between from about 0.1 to about 1, with about 0.25 to about 1 typically being preferred. Reference herein to a particular silicate composition having an "underexchanged" silicate, silicate matrix, or related phrase means that the molar amount of the onium salt is generally less than the molar amount of the exchangeable ionic sites in the silicate. In embodiments of the invention in which the silicate composition includes more than one onium salt and optionally more than one type of inorganic layered silicate, it will be understood that the exchange reference is made with respect to all the onium salts and all the layered silicates in the composition.

Preferred high temperature organic surfactants will include at least one onium salt suitable for high temperature use. Preferably, all the onium salts in the surfactant are suitable for use at the high temperature. As discussed, a particular onium salt is a phosphonium salt which salt can be alone or in combination with at least one other

onium salt such as the sulfonium salt and the ammonium salt. A more particular ammonium salt is an alkyl ammonium salt such as those referenced below. In embodiments of the invention in which silicate composition includes the alkyl ammonium salt, that salt is preferably underexchanged although for some applications it may be useful to overexchange that salt for the exchangeable silicate.

Further provided by the invention are compositions that include at least two of the inorganic layered silicates disclosed herein, preferably between from one to about five of the silicates and more preferably about two of such inorganic layered silicates.

Such compositions find use in a variety of settings including those requiring a combination of inorganic layered silicates to achieve a desired performance result.

Also provided by this invention are silicate compositions that include at least one of the inorganic layered silicates and at least one organically modified layered aluminosilicate (hereinafter "ORMLAS"). Particular silicate compositions include between from one to about 5 of the inorganic layered silicates, preferably one of same, and between from one to about 5 ORMLAS, preferably one of same. Thus it is an objective of this invention to provide silicate compositions that include a mixture of silicate types including those with one type of inorganic layered silicate type and one type of ORMLAS.

Unless stated otherwise, reference herein to "ORMLAS" is meant to encompass one type of organically modified layered aluminosilicates.

In another aspect, the present invention provides particular silicate compositions referred to as nanocomposites. In one embodiment, the nanocomposites include at least one of the inorganic layered silicates discussed herein or at least one of the ORMLAS. In this example of the invention, the nanocomposite also includes at least one suitable polymer material. Alternatively, the nanocomposite can include at least one of the inorganic layered silicates and at least one of ORMLAS and at least one desired polymer material. As discussed below, preferred nanocomposites have a heat distortion temperature of at least about 150°C.



Use of particular components in a nanocomposite or other silicate composition of this invention will be guided by several parameters including the specific performance characteristic(s) desired, and intended use.

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As mentioned, a wide spectrum of polymer materials are compatible with the silicate compositions provided by this invention. More specific polymer materials include those appropriate for intercalation within layers of the inorganic silicate. Preferred are polymer materials capable of providing a d-spacing between silicate layers of at least about 18 Angstroms as determined by conventional X-ray diffraction (XRD). For disclosure relating to XRD, see X-ray Diffraction Methods in *Polymer Science*, L. E. Alexander, Wiley, N.Y., pp. 137-229 (1969), hereby incorporated by reference.

Thus, in one embodiment, the invention provides silicate compositions and especially nanocomposites that exhibit a d-spacing between the silicate layers of at least about 18 Angstroms, preferably at least about 18 to about 19 Angstroms. Preferred inorganic layered silicates for use in this embodiment of the invention are well-suited for intercalating polymer material, including multiple polymer materials.

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Additional nanocomposites of the invention include at least one of the inorganic layered silicates disclosed herein and at least one of the polymer materials. More particular polymer materials suited for use in this embodiment include those appropriate for exfoliation of layers of the silicate. In this example of the invention, the nanocomposition exhibits a preferred d-spacing between silicate layers of at least about 18 Angstroms as determined by the XRD with between about 18 to about 19 Angstroms often being preferred.

As discussed, many preferred silicate compositions in accord with this invention will be acceptable for long-term or short-term use in excess of about 150°C. Especially preferred nanocomposites will be suited for long-term or short-term use at a high temperature of at least about 200°C with at least about 250°C to about 400°C

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being preferred for many applications. Methods for detecting and quantifying a wide variety of parameters relating to thermal stability are known in the field and include conventional heat distortion tests.

5           Additionally preferred silicate compositions include those nanocomposites that having good or "high" barrier properties. In this embodiment of the invention, the nanocomposites typically provides for the good barrier properties at temperatures below about 150°C. High barrier properties are especially useful when the silicate composition is included in at least part of a manufactured article including up to  
10 essentially the entire article. As will be appreciated, the performance characteristics of many manufactured articles such as those relating to the automotive, aerospace, electronic, pharmaceutical, apparel, food and beverage packaging industries will be enhanced by having good barrier properties to a solute such as a liquid, gas; or mixture thereof.

15           More particular nanocomposites suitable for use in the manufactured articles help provide for a significant permeability barrier to diffusion of at least one of: oxygen, nitrogen, carbon dioxide, water vapor, a noble gas such as helium; or a mixture thereof. This feature of the invention has many advantages including  
20 providing manufactured articles with capacity to reduce or eliminate gas diffusion as determined by standard testing procedures described below.

          More particular examples of the manufactured article include or consist of those having an enclosed space with a gaseous, solid or semi-solid material intended  
25 to be essentially confined in that space. In this embodiment, the manufactured article may include or consist of a structure that is particularly designed to exclude or retain a material such as a liquid, gas; or mixture thereof. Particular structures are referred herein as a "cushion", "bladder", "bag" "pillow" "base insert" or like term to denote intention to reduce or eliminate impact force to which the manufactured article may  
30 be exposed during construction or use.

Preferred bladders are gas bladders that include at least one gas enclosed by at least one of the silicate compositions of this invention. Preferred gas bladders provide several uses and advantages including improved impact absorption, directional stabilization, and lightness, particularly when used in footwear applications.

Future nanocomposites in accord with this invention include those well-suited for use in pharmaceutical packaging materials such as "blister packs". In this embodiment, the blister pack is preferably adapted to hold a pharmaceutical composition (e.g., a pill) and can significantly exclude (or retain) the solute from the composition.

Additionally preferred silicate compositions and particularly nanocomposites will exhibit at least one of the following performance characteristics: good thermal stability, excellent heat distortion temperature, suitable mechanical strength, good interfacial design, and polymer compatibility. Additionally preferred are nanocomposites that have favorable interlayer d-spacing for those embodiments in which intercalation of the polymer material is useful.

Also preferred are nanocomposites featuring at least one of the following particular performance characteristics: good impact resistance, excellent tensile modulus, good flame resistance, and suitable glass transition temperature. Especially preferred are nanocomposites featuring at least two of these characteristics and more preferably most or all of them. As mentioned, presence of one or more of the performance characteristics in a particular nanocomposite will be guided by several parameters including intended use.

As discussed, the silicate compositions of this invention provide many significant uses include use in more particular articles of manufacture. Illustrative of such articles include those mentioned above and including these suitable for use in the container (e.g., beverage) clothing and footwear industries.

In another aspect, the present invention provides highly useful ORMLAS and ORMLAS related materials. Particular ORMLAS of interest include at least one inorganic layered silicate, preferably a synthetic inorganic layered silicate; and at least one organophilic agent, preferably an organic compatibilizing agent, covalently  
5 attached to the layered silicate. Preferably, the inorganic layered silicate has an aspect ratio of from between about 10 to about 1000 as determined by transmission electron microscopy (TEM).

Additionally preferred ORMLAS are made by the "sol-gel" synthetic process  
10 discussed below.

Additionally preferred ORMLAS feature a d-spacing between the silicate layers of at least about 20 Angstroms.

15 The invention further provides a composition that preferably includes between from about two to about five ORMLAS, more preferably about two ORMLAS. For many applications, a silicate composition that includes one ORMLAS will be useful.

Preferred inorganic layered silicates for use in accord with this invention are  
20 generally negatively charged clay minerals that can undergo isomorphous ion exchange. The silicates generally differ from one another in characteristic properties such as particle size, density and distribution of negative charges. More specific silicates are naturally-occurring or synthetic clay or clay-related minerals. Many silicates can be readily obtained from commercial vendors.

25 More preferred clay minerals for use with this invention are fully compatible with a pre-determined polymer material and are particularly amenable to high temperature use or processing steps.

30 In some embodiments of this invention such as those involving ORMLAS, use of chemically modified silicates will be generally preferred. In a particular

embodiment, that chemical modification is covalent bonding between the silicate and at least one suitable organophilic agent, preferably at least one compatibilizing agent.

Preferred organophilic agents are often referred to herein as "compatibilizing" agents to denote capacity to provide good contact between layered silicates and polymer material. A more preferred compatibilizing agent is generally appropriate for high temperature applications and facilitate combination of the silicate and the polymer material as a single compound. Additionally preferred compatibilizing agents optionally help to optimize d-spacing between intercalated silicate layers to a particular value or range of values as required.

More specifically preferred compatibilizing agents for use with the inorganic layered silicates of this invention include at least one of an onium salt as discussed previously or an organo-silane. Preferred onium salts include sulfonium, phosphonium and ammonium. Preferred organo-silane compounds include those materials which can render an ORMLAS thermally stable and significantly organophilic. Illustrative organo-silane compounds include organically functionalized silanes and particularly alkylsilanes and alkoxy silanes. As discussed below, it has been found that modification of the organo-silane, i.e., by introducing non-aliphatic groups can facilitate production of silicate compositions with very useful performance characteristics.

In a particular embodiment of this invention, the nanocomposite includes at least one ORMLAS disclosed herein, preferably one ORMLAS and at least one suitable polymer material including a polymer blend or alloy. In a more particular embodiment, the polymer material is well-suited to intercalate within layers of the ORMLAS. Alternatively, the polymer material can be selected for exfoliation of layers of the silicate. The nanocomposite can optionally include at least one of the inorganic layered silicates disclosed herein, e.g., to enhance or to provide for one or more desired performance characteristics.

Also envisioned is a nanocomposite that includes matrix regions in which the polymer material is intercalated and other regions in which the silicate layers are essentially completely exfoliated within the polymer matrix.

5 As will be understood to those of skill, choice of a particular component or group of components for use in a desired silicate composition will be guided by recognized parameters including intended use and the performance characteristic(s) desired. More specific component choices will be guided by at least one of the following considerations: thermal stability, barrier property, and mechanical strength.

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In another aspect, the invention provides a range of manufactured articles that include or consist of at least one of the silicate compositions disclosed herein. In one embodiment, the article includes at least one of the nanocomposites, preferably between from 1 to about 5 nanocomposites, with one nanocomposite being preferred  
15 for many uses. In a more particular embodiment, the article is capable of posing a significant permeability barrier to diffusion of at least one of the following: oxygen, nitrogen, carbon dioxide, water vapor, a noble gas; or a mixture thereof. Preferably, the noble gas is helium. Highly preferred manufactured articles include or consist of those nanocomposites and other optimally silicate compositions that can confer the  
20 barrier properties as well as other desired performance characteristics.

More preferred is an article of manufacture that includes at least one of the silicate compositions and particularly at least one of the nanocomposites disclosed herein, which article has a preferred permeability to oxygen of at least about 1.5 to  
25 about 2-fold lower than the oxygen permeability of the neat polymer. Of course, in embodiments in which the polymer material is a mixture such as a polymer blend or polymer alloy, meaningful comparisons will often be made between the article made with the polymer mixture instead of the neat polymer.

30 Additionally preferred articles of manufacture include those silicate compositions that can provide relatively lightweight characteristics as that term is

understood in this field when compared to the same or related article employing prior silicate compositions.

In another aspect, the invention provides a variety of useful methods for making an inorganic layered silicate as provided herein. Preferably, that silicate includes non-covalently bound thereto at least one of the organophilic agents mentioned and possibly at least one high temperature organic surfactant. In one embodiment, the method includes at least one and preferably all of the following steps:

- a) admixing the inorganic layered silicate in a suspension of aqueous or organic solvent,
- b) contacting the solution with the surfactant under conditions which enable formation of a precipitate in the solution; and
- c) collecting the precipitate from the solution in which the precipitate includes the inorganic layered silicate non-covalently bound to the high temperature organic surfactant.

In one embodiment of the method, the surfactant comprises at least one onium salt as discussed previously. Preferably, the method involves use of at least one phosphonium salt and preferably one phosphonium salt.

In another embodiment, the surfactant comprises at least one ammonium salt, preferably an alkyl ammonium salt. In a more preferred embodiment the molar amount of the onium salt is less than the molar amount of the exchangeable ions in the silicate. Methods for determining the exchangeable ions include the conventional ion exchange methods discussed above.

In a more particular embodiment of the method, the surfactant includes a combination of acceptable onium salts, preferably at least one of a suitable phosphonium salt, and an ammonium salt, preferably an alkyl ammonium salt.

In another aspect, the present invention provides methods for making the nanocomposites disclosed herein. In one embodiment, the methods include combining at least one inorganic layered silicate with at least one suitable polymer material. Preferred combination involves polymer intercalation or exfoliation within  
5 layers of the inorganic layered silicates. Preferred nanocomposites for use in the method include those mentioned previously.

More particular methods for making the nanocomposites are discussed below. Such methods include polymer melt and solution based methods that in optimal  
10 practice help to manifest the performance characteristics desired.

In another aspect, the invention provides methods for making an organically modified layered aluminosilicate (ORMLAS). In one embodiment, the method includes at least one and preferably all of the following steps:  
15 a) combining in a basic and alcoholic aqueous solution at least one metallic halide (e.g., Al, Mg, Ni, or Fe halide) with at least one organo-siloxane represented by the following general formula I:



in which R1 is a substituted or unsubstituted alkyl, alkenyl, alkynyl, or alkoxy group, and each of R2, R3, and R4 is independently an alkoxy group the same or different,

b) producing a precipitate in the solution; and  
30 c) collecting the precipitate from the solution in which the precipitate includes the ORMLAS.



In one embodiment, the method preferably includes combining in the solution at least one organo-siloxane having at least one carbon chain shorter than the organo-siloxane of Formula I. By the term "shorter" is meant that the organo-siloxane has fewer carbon atoms than the organo-siloxane of Formula I, generally from between  
5 one to about 10 carbon atoms shorter.

In another embodiment of the method, the organo-siloxane of Formula I preferably includes at least one substituted or unsubstituted alkyl group. In this example of the invention, the method further includes combining in the solution at  
10 least one organo-siloxane as represented in Formula I except that the organo-silane will include at least one non-aliphatic group.

The foregoing method is generally flexible and can be readily modified to suit intended use. For example, the method can be used with one organo-silane or a  
15 combination thereof e.g., to achieve a desired performance characteristic.

The invention also provides more specific methods for making a nanocomposite in which an extruder or related implementation is preferably employed. In one embodiment, the methods include at least one and preferably all of  
20 the following steps:

- a) combining in a suitable extruder at least one inorganic layered silicate disclosed herein, e.g., one ORMLAS, with at least one polymer material, the combining being under conditions which enable melting of the polymer material in the extruder,
- 25 b) adding the inorganic layered silicate to the melted polymer material in which the addition is under conditions which enable effective contact between the layered silicate and the polymer material,
- c) mixing the inorganic layered silicate and the melted polymer material; and
- 30 d) producing the nanocomposite from the extruder.

In one embodiment, the method includes use of between from one to about five of the inorganic layered silicates disclosed herein. However, for most applications, use of one of the silicates, ie., one of the inorganic layered silicates or one ORMLAS will be preferred. In this example, the inorganic layered silicate  
5 preferably includes at least one of the high temperature organic surfactants non-covalently attached to the silicate. Preferred surfactants are the phosphonium salt alone or in combination with at least one other onium salt, e.g, sulfonium salt, ammonium salt and preferably alkyl ammonium salt.

10 In another embodiment, the method includes use of between from one to about five ORMLAS with one of the ORMLAS being preferred for many applications. In this example of the invention, the ORMLAS preferably includes at least one of the organic compatibilizing agents discussed previously. In a further embodiment of this method, ORMLAS can be optionally combined in the extruder with between from one  
15 to about five of the inorganic layered silicates and preferably one of the silicates disclosed herein.

Components for use in the extruder method can be added to the extruder together or separately as needed. The order in which the extruder components are  
20 combined is not critical provided that the nanocomposite has the desired performance characteristics.

In another embodiment, the invention provides solution based methods for making the silicate compositions described herein and particularly certain  
25 nanocomposites. In general, such solution based methods will often be appropriate in settings where the desired polymer material produces noxious gas and/or where use of a specific polymer material at the high temperature may pose risk to personnel. Such methods are additionally preferred when very good dispersion of the clay minerals is required.

30 More particularly, the invention provides solution based methods for making the nanocomposite that include at least one and preferably all of the following steps:

- a) contacting at least one clay mineral with a solvent suitable for the polymer material selected,
- b) exposing the solution to ultrasound conditions sufficient to suspend the clay mineral in the solvent,
- 5 c) contacting the solution with at least one polymer material in which the polymer material is preferably in liquid form,
- d) mixing the suspension and the polymer material for at least several hours up to a few days; and
- 10 d) removing the solvent from the suspension to produce the nanocomposite, e.g., in a film or related form.

Additional methods for making the silicate compositions are provided below and include methods involving multiple processing techniques. In general, the techniques are formulated to enhance desired performance characteristics including  
15 long-term high temperature use. For example, practice of the foregoing methods is assisted by innovative chemical design of the organic-inorganic interface in the compositions to be made. In preferred embodiments, the methods employ more thermally stable surfactants/compatibility agents, and more thermally stable synthetic organically-modified layered-silicate reinforcements to make the silicate  
20 compositions. These approaches are compatible with several synthetic manufacturing methods including the solution-based methods and solvent-free melt or melt-related techniques discussed above.

The invention also provides more specific polymer melt process conditions for  
25 making (compounding) various nanocomposites in accord with this invention. For example, in a more specific embodiment, the methods include at least one and preferably all of the following steps:

- a) feeding components to be compounded into a suitable extruder implementation such as a single screw extruder and preferably a twin-screw extruder, in which the components are fed at a pre-determined  
30 rate, the feeding being under conditions that enable the neat polymer material to achieve essentially melt temperature therein,

- b) combining the components inside the extruder under conditions that enable efficient mixing therebetween and reduce or eliminate any trapped gas; and
- c) producing the nanocomposite from the extruder implementation.

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More particular process conditions for compounding the nanocomposites of this invention are provided below. Choice of particular components to use in the method as well as more specific feeding and combining steps will be guided by intended use of the nanocomposite to be made including the performance characteristics desired.

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As discussed, the invention provides a wide variety of specific articles of manufacture that preferably include at least one of the nanocomposites disclosed herein. More preferred articles include from one to about five of the nanocomposites with one of the nanocomposites being useful for most applications. In a preferred embodiment, the article is footwear adapted for athletic or related use.

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In another aspect, the invention includes methods for making a manufactured article that includes at least one of the nanocomposites provided by this invention. In one embodiment, the methods include adding at least one nanocomposite to at least one component intended for the article and assembling the component to make the article. Preferred methods involve making footwear adapted for athletic use.

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In addition to the foregoing, the invention provides additional uses and advantages which will be apparent to those with skill in this field.

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For example, in particular embodiments, the invention is fully compatible with use of essentially environmentally-friendly and solvent-free polymer melt processing techniques.

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In addition, many of the present silicate compositions including particular nanocomposites feature thermally stable natural clay systems having, e.g., organic phosphonium surfactants

5           Still further, the invention helps to solve several problems that have plagued prior attempts to make and use silicate compositions effectively. In particular, many prior nanocomposites have been found to exhibit undesired plasticization. This problem can be substantially reduced or even totally avoided by significantly lowering the organic content of the clays employed in the composition. That is by  
10 lowering the organic content of the nanocomposite by between from about 10% to about 90% relative to the organic content of recognized alkyl ammonium nanocomposites, the plasticization can be avoided. The silicate compositions of this invention and particularly the preferred nanocomposites substantially avoid undesired plasticization.

15           In particular, the invention avoids undesired plasticization in several ways. For example, it provides methods that can reduce this phenomenon by using partial replacement of non-aliphatic groups for the long chain alkyls typically used to make the compositions. This approach can be adapted for use with the phosphonium  
20 exchanged clays for which a lower than 100% exchange capacity is often useful. It is believed that these and other methods disclosed herein can provide a silicate composition and particular a nanocomposite that has a higher heat distortion without unduly compromising the  $T_g$  due to plasticization.

25           Also, it is believed that many nanocomposites of this invention including those that employ underexchanged clay will be significantly superior to compositions that include the overexchanged clays.

          These and other advantages facilitate use of the invention in a variety of  
30 settings. For example, the ORMLAS generally include "built-in" surfactants that help to minimize or eliminate presence of harmful alkyl ammonium surfactants. These advantages facilitate use of nanocomposites and related silicate compositions in

important applications such as in food or beverage packaging materials. In preferred embodiment, the invention thus provides recyclable and more cost-effective packaging materials that find use in the replacement of previously unrecyclable multilayer plastic packages.

5

The invention also provides nanocomposites featuring a good barrier to at least one of a gas or liquid solute. In one embodiment, the invention provides what is sometimes referred to herein as a "high barrier" nanocomposite or a related phrase. In this example of the invention, the nanocomposite decreases the transmission rate of the solute through the nanocomposite as determined by standard testing procedures. Such nanocomposites have a wide spectrum of useful applications including use in manufactured articles in which good retention or exclusion of the solute is desired. In one embodiment, the manufactured article includes or consists of at least one of the nanocomposites provided herein and possesses an effective permeability barrier to the solute.

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As will be discussed below, such high barrier nanocomposites have a wide variety of useful applications including use in manufactured articles such as "blister" or "bubble" packs.

20

In another aspect, the invention relates to the preparation of polyolefin layered silicate polymer nanocomposite materials. In one embodiment, the materials include suitable amounts of at least one of and preferably all of the following: polyolefin; polyamide, what is referred to herein as "functionalized grafted polyolefin", organoclay, and synthetically formulated organoclay preferably formed by self-assembly techniques. In this example of the invention, the functionalized grafted polyolefin typically plays the role of a compatibilizer in embodiments in which polyolefin and polyamide phases are non-compatible particularly in certain compounding blends.

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These and other uses and advantages of the invention will become more apparent from the following disclosure including the drawings, examples and the claims.

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**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1A is a schematic drawing showing a prior inorganic layered silicate with alkyl ammonium surfactant.

- 5            Figure 1B is a schematic drawing showing an inorganic layered silicate of the invention with tetraphenyl phosphonium surfactant.

Figure 1C is a schematic drawing of an ORMLAS.

- 10           Figure 2 is a chemical representation of tetraphenyl phosphonium surfactant.

Figure 3 is a schematic drawing of types of polymer-layered silicate nanocomposite structures.

- 15           Figure 4 is a table of recognized properties of nylon-6 and layered silicate-nylon nanocomposites. See Giannelis, E.P. (1996), as discussed *infra*.

Figure 5 is a graph showing an X-ray Diffraction (XRD) pattern for aluminooctylsilsesquioxane (C<sub>8</sub>ORMLAS).

20

Figure 6 is a graph showing an XRD pattern for aluminododecylsilsesquioxane (C<sub>12</sub>ORMLAS).

- 25           Figure 7 is a graph showing an XRD pattern for aluminooctadecylsilsesquioxane (C<sub>18</sub>ORMLAS).

Figure 8 is a transmission electron microscopy (TEM) image of Al-dodecylsilsesquioxane (C<sub>12</sub>ORMLAS).

- 30           Figure 9 is TEM image of Al-Octadecyl Silsesquioxane (C<sub>18</sub>ORMLAS)/Ultem Nanocomposite.



Figure 10 is a TEM image of tetraoctyl phosphonium Exchanged Clay/Ultem Nanocomposite

Figure 11 is a TEM image of Atapulgit/Ultem Nanocomposite.

5

Figure 12 is a table showing a list of alkyl and phenyl ORMLAS materials along with observed d-spacings.

Figure 13 is a graph showing thermo-gravimetric analysis (TGA) of dodecyl silsesquioxane under nitrogen atmosphere.

10

Figures 14A-G are XRD results for selected Al-silsesquioxanes.

Figures 15A-C are powder XRD patterns of (15A) 5 wt.% Al n-Dodecyl silsesquioxane with Nylon powder before extrusion, (15B) 7 wt. % Al n-Dodecyl silsesquioxane with Nylon powder before extrusion, and (15C) 7% Al n-Dodecyl silsesquioxane-Nylon nanocomposite formed after extrusion.

15

Figures 16A-B are TEM images showing exfoliation of Al-dodecylsilsesquioxane nylon nanocomposite.

20

Figures 17A-B are graphs showing Differential Scanning Results (DSC) of Nylon-6 and Nylon ORMLAS compositions.

Figures 18A-C are graphs showing XRD spectra for montmorillonite ion-exchanged with various phosphonium cations.

25

Figures 19A-B are graphs showing XRD patterns of extrusion product of various phosphonium exchanged clay and Nylon nanocomposites.

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Figure 20 is a graph showing DMA curves for a) neat Udel and b) Udel nanocomposite.

Figure 21 is a graph showing results of a dynamic mechanical analysis for Nylon-6 and Nylon 6 -ORMLAS nanocomposite.

- 5        Figures 22A-C are graphs showing thermal stability of various materials. Fig. 22A Dihydrotrallowdimethyl ammonium exchanged montmorillonite; Fig. 22B. Tetraoctyl phosphonium exchanged montmorillonite; Fig. 22C) aluminum octadecyl silsesquioxane (C<sub>12</sub> ORMLAS).
- 10        Figure 23 is a schematic drawing showing a high barrier nanocomposite of this invention. In the drawing, layered silicate is shown as a plurality of horizontal lines embedded in polymer material. Retarded solute movement through the nanocomposite is exemplified by the arrow.
- 15        Figure 24A-B are graphs showing X-ray Diffraction (XRD) patterns. Figure 24A is an XRD of exchanged Na<sup>+</sup>-montmorillonite. Figure 24B to XRD of exchanged Na<sup>+</sup>-montmorillonite.
- 20        Figure 25A-B are graphs showing X-ray Diffraction (XRD) patterns. Figure 25A is an XRD of 5% Clay-PET nanocomposite. Figure 25B is an XRD of 10% Clay-PET nanocomposite.

#### **DETAILED DESCRIPTION OF THE INVENTION**

- 25        As discussed, the present invention features a wide spectrum of compositions that include at least one type of inorganic layered silicate and at least one type of organophilic agent associated with the silicate. That association is preferably through covalent or non-covalent bonding between the agent and the silicate layer. In one embodiment, the invention provides inorganic layered silicates that include at least one non-covalently bound high temperature organic surfactant which surfactant
- 30        includes at least one onium salt. Additionally provided are organically modified layered aluminosilicates (ORMLAS) that include at least one covalently attached organic compatibilizing agent. In more particular embodiments, the invention

provides a range of highly useful nanocomposites that include at least one of the inorganic layered silicates and optionally at least one of the ORMLAS which nanocomposite further includes at least one suitable polymer material. Alternatively, the nanocomposites include at least one ORMLAS and optionally at least one of the inorganic layered silicates with the polymer material.

In general, the silicate compositions feature exceptional performance characteristics such as better thermal stability, good mechanical strength and favorable gas barrier properties with respect to a solute such as a gas, liquid, or mixture thereof. Of particular interest are those nanocomposites that have at least one of these properties as well as more specifically desirable performance characteristics such as long-term high temperature use.

The present invention provides a variety of high temperature and lightweight silicate compositions that have highly useful applications. The invention provides many useful alternatives to the prior practice of making silicate compounds which has typically involved use of alkyl ammonium salts and related agents. As discussed, the alkyl ammonium salts may not always provide silicate compositions with optimal performance characteristics.

For example, in one embodiment, the invention provides new silicate compositions and particularly nanocomposites with exceptional long- or short-term high temperature use. The compositions typically include the polymer material with at least one compatibilizing agent covalently linked to the silicate structure (ie., an ORMLAS). By covalently linking the compatibilizing agent to the layered silicate structure in accord with this invention, better performance characteristics can usually be achieved. In contrast, many prior silicates employ non-covalently bound alkyl ammonium salts which do not always provide these characteristics.

In addition, the invention provides silicate compositions and particularly nanocomposites that include at least one onium salt and especially the phosphonium salt alone or in combination with at least one other onium salt. In a particular

embodiment, it has been found that non-covalently linking the phosphonium salt to the silicate layer generally improves performance characteristics and provides for better synthesis of the silicate composition.

5 Unless otherwise indicated, the term "high temperature" or related phrase when used to reference a silicate composition of this invention will be understood to mean a preferred temperature of at least about 150°C, preferably between from about 200°C to 450°C, and more preferably between from about 250°C to about 400°C.

10 As also discussed, the invention provides highly useful synthetic methods for making the silicate compositions of this invention. As an illustration, the invention provides two essentially direct melt processible techniques for making the preferred nanocomposites. Practice of these methods can enhance performance characteristics including the thermal stability from prior limits of about 150°C, to about 250°C -  
15 300°C up to about 400°C.

Further provided are several methods for making ORMLAS that generally involve combining specific layered silicates and the organic compatibilizing agent in a single chemical compound. This aspect of the invention renders the ORMLAS  
20 thermally stable, exceptionally organophilic and compatible with a range of suitable polymer materials. It is believed that the ORMLAS and ORMLAS-related compositions provided by this invention include some of the most thermally stable silicate-organic interfaces known in the field. Significantly, the ability of the present methods to form layered structures with the facilitates effective use of this invention  
25 in a wide variety of applications.

By the term "ORMLAS-related" composition is meant ORMLAS plus at least one inorganic layered silicate as provided herein.

30 See Examples 1-2 below describing how to make and use a variety of ORMLAS.

In particular, it will be readily apparent that the recognized stability of Si-C bonds provides an effective chemical framework for using the silicate compositions in settings where superior performance characteristics are needed.

5       As discussed, specific silicate compositions of this invention can be manufactured from one or a combination of clay minerals including what is referred to in the field as hard clay, soft clay, talc; or a mixture thereof. Preferred clay minerals include naturally-occurring or synthetic clay as well as clay mixtures. In  
10       embodiments in which the silicate composition includes at least one naturally-occurring clay, characteristics of the clay can be modified by non-covalently associating therewith at least organophilic agent and preferably at least one of the high temperature use surfactants discussed previously.

      More preferred layered materials for use in this invention may vary widely but  
15       generally include phyllosilicates and related materials. Illustrative materials are smectite clay minerals such as montmorillonite, nontronite, sepiolite, atapulgite, beidellite, volkonskoite, hectorite, saponite, sauconite, magadiite, and kenyaite; vermiculite; and the like. Other useful layered materials include illite minerals such as  
20       ledikite and admixtures of illites with the clay minerals. Other useful layered materials, particularly useful with anionic polymers, are the layered double hydroxides. See e.g., W. T. Reichle, *J. Catal.*, 94 (12985) 547). Many of these clays have positively charged layers and exchangeable anions in the interlayer spaces. Additional phyllosilicates include the 2:1 type having a negative charge on the layers  
25       ranging from about 0.25 to about 0.9 charges per formula unit and a commensurate number of exchangeable cations in the interlayer spaces. More preferred layered materials are smectite clay minerals such as montmorillonite, nontronite, beidellite, bolkonskoite, hectorite, saponite, sauconite, sepiolite, fluorohectorite, atapulgite, laponite magadiite, and kenyaite. Generally preferred smectites include aluminosilicates, magnesianosilicates as well as mixtures thereof. See also U.S. Pat. No.  
30       5,385,776 for other clay minerals suitable for use with this invention.

The amount of clay mineral used in a silicate composition of this invention will vary depending on intended use and particularly by the performance characteristics desired. For example, an amount of clay mineral (or combination of clay minerals) less than about 0.5% by weight of the matrix will be useful for many applications. For other applications however, the amount of clay mineral may approach several parts per million or less. Preferably the amount of a particular clay mineral in a silicate composition will be from between about 0.1% by weight to about 10% by weight with between from about 0.1% by weight to about 0.5% by weight of the matrix being preferred for many applications.

More particularly preferred is clay levels from about ppm level up to about 10% clay in the polymer matrix.

Preferred polymer materials for use in the present invention are substantially intercalated within the inorganic layered silicate or exfoliated as discussed previously. More particular layered silicates are often in the form of platelet particles. As used herein, "platelet particles" are particles that usually have two relatively flat opposite faces wherein the thickness of which is the distance between the faces, which is relatively small compared to the size of the faces.

Preferred platelet particles in accord with this invention typically have the thickness of the individual layers in the silicate, or small multiples less than about 10, preferably less than about 5 and more preferably less than about 3 of the layers, and still more preferably 1 or 2 layers. The other dimensions of the platelet particles may vary greatly depending on intended use and the specific performance characteristics desired. However in embodiments employing the clay minerals, preferred particle faces are roughly round or oblong having average diameters between about 10,000 Angstrom and about 50 Angstrom, such that the aspect ratio length/thickness ranges from about 1000 to about 1.

For the purposes of the present invention, the average diameter is defined as the diameter of a circle having an area equal to the surface area of one broad surface

face of the platelet shaped particle. The average diameter is determined from particle surface area by standard methods such as use of an appropriate analyzer system. In the preferred embodiments of the invention, the average thickness of the platelet particles is equal to or less than about 20 Angstrom with a maximum thickness of 50 Angstrom and the average diameter is between 5,000 Angstrom and 100 Angstrom with a maximum diameter of 10,000 Angstrom. More preferably, the average thickness is equal to or less than about 15 Angstrom with a maximum thickness of 25 Angstrom and the average diameter is from about 2,000 Angstrom to about 200 Angstrom with a maximum diameter of 5,000 Angstrom. Even more preferably, the average thickness is from about 1 to about 15 Angstrom with a maximum thickness of 25 Angstrom and the average diameter is from about 2000 Angstrom to about 200 Angstrom with a maximum diameter of 5,000 Angstrom.

A still more preferred clay mineral for use with the present invention has an aspect ratio of between from about 50 to about 1000 and more preferably a thickness of about 1nm. As mentioned, naturally-occurring clay minerals exchanged with at least one onium salt, preferably a phosphonium salt alone or in combination with at least one of an alkyl ammonium or sulfonium salt are often preferred.

More particular examples of the foregoing include preferred phosphonium exchanged montmorillonite clays provided below in Example 3. These particular silicate compositions include phosphonium salts having organophilic moieties such as long chain alkyl and aryl groups. It has been found that use of phosphonium salts with the organophilic moieties positively impacts the invention in several respects including improving contact between the inorganic layers and a wide range of polymer materials. That is, the inorganic layered silicate "looks" more like the polymer material for which effective intercalation or exfoliation is desired.

Additionally preferred are layered silicates that have been chemically modified with at least one compatibilizing agent as provided herein. For example, use of long chain alkyls in the synthesis of ORMLAS usually improved dispersion within polymer materials such as Ultem.

Particular phosphonium clays of this invention can be synthesized with alkyl groups that are longer than those used in the field. Preferred are longer alkyl groups that help to "prop" the silicate layers apart better (ie. give enhanced d-spacing), thereby allowing for better intercalation / exfoliation with the various polymers, polymer blends or polymer alloys.

By the term "compatibilizing agent" or related phrase is meant a preferred organophilic agent that is capable of being covalently linked to the inorganic layered silicate and which facilitates effective intercalation or exfoliation in that silicate. A particular agent is "compatible" to the extent that it facilitates favorable interactions between the platelet particles and the matrix polymer material. Without wishing to be bound to theory, especially preferred compatibilizing agents in accord with this invention are believed to provide for at least one of the following desirable matrix properties: similar cohesive energy densities for the polymer material and the derivatized platelets, similar or complimentary capacities for dispersive, polar, or hydrogen bonding interactions, or other specific interactions, such as acid/base or Lewis-acid/Lewis-base interactions. Additionally, good compatibilization helps to improve contact and particularly dispersion of the platelet particles in the matrix and an improved percentage of delaminated platelets with a thickness of less than about 50 Angstrom.

It is one achievement of this invention to enhance incorporation of layered silicates and clay minerals with desired polymer materials, thereby providing silicate composition with superior performance characteristics.

As discussed, particular inorganic layered silicates of this invention include at least one high temperature organic surfactant non-covalently attached to the silicate in which the surfactant includes at least one phosphonium group. By the term "high temperature organic surfactant" or related phrase is meant thermal stability to decomposition to at least about 200°C. The inorganic layered silicates having the



surfactant have a preferred d-spacing of from between about 10 to about 50 Angstroms as determined by XRD or a related test.

Preferred silicate compositions of this invention and particularly the disclosed  
5 inorganic layered silicates and ORMLAS are compatible with a wide variety of polymer materials.

More particular polymer materials are polymers such as those suitable for  
polymerization with a wide variety of clay minerals. Preferred polymers can be  
10 adapted in accord with this invention for long-term high temperature use.  
Additionally preferred are polymers that provide at least one of good thermal stability,  
excellent mechanical strength, and good barrier properties as disclosed herein.  
Additionally preferred polymers are generally compatible with a wide variety of melt  
and solution processing techniques.

15 More specific polymers include but are not limited to high temperature  
polymers such as thermoplastic polymers, e.g., thermoplastic polyesters. Illustrative  
of such polyesters include liquid crystalline polymers such as wholly aromatic  
polyesters and copolyesters such as Xydar™ and Vectra™, PET (polyethylene  
20 tetraphthalate), PBT, poly(butylene tetraphthalate), PPS (polypropylene sulfide), and  
PCT (polycyclohexylene dimethylene tetraphthalate). Additionally suitable  
thermoplastic polymers include polyethylene, polypropylene (PP), polystyrene,  
polyvinylchloride (PVC), PVDC, and polyamides such as Nylon and particularly  
specific Nylon types such as polyamide 11, 12, 4/6, 6/6 and 6/10. Additionally  
25 suitable are thermoplastic elastomers such as elastomers of polyurethane, and  
Hytrel™. Also contemplated are blends and alloys of the foregoing specific polymers.

Additionally, preferred are polyamide, polyolefin, polyetherimide (PEI),  
thermoplastic polyimide, polysulfone, polyurethane, copolyester copolymer,  
30 polypropylene (PP), polycarbonate (PC), copolyane elastomer (butylene, poly  
(alkylene ether) phthalate plus stabilizer) or a blend or an alloy thereof.

Also suitable polymers for use with this invention include Texin™, (polyurethane (PU)), Udel (polysulfone (PSU)), Vectra A™ or Vectra B™ (liquid crystal polymer (LCP)), Ultem™ (polyetherimide), ethylene vinyl alcohol (EVOH); polyphtalamide (PPA) (polyphenylene sulfide (PPS)); or a blend or an alloy thereof.

5

Additionally suitable polymer materials suitable for use with this invention include those disclosed in U.S. Pat. Nos. 5,514,734, 5,747,560, and 5,866,645, the disclosures of which are incorporated herein by reference.

10

A preferred polymer for many applications including those involving use in a manufactured article requiring a cushioning or gas bladder structure is Hytrel or a blend or alloy thereof. A preferred Hytrel is Hytrel 5526, Hytrel 5612, Hytrel 4056, Hytrel 5526, and Hytrel 5612; or a mixture thereof.

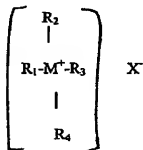
15

See also Kaplan, W. ed in *Modern Plastics Encyclopedia* (1999) (McGraw-Hill Companies, NY) for more detailed information relating to the foregoing and other acceptable polymer materials for use with this invention.

20

In particular embodiments of this invention, the high temperature organic surfactant includes an onium salt preferably having the following general formula II:

25



II

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wherein M is one of N, S, O or P atom,  
each of R1, R2, R3 and R4 is independently an optionally substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl,

alkylaryl, alkenylaryl, alkynylaryl, alkylthio, alkylsulfinyl, alkylsulfonyl, or carboxycyclic aryl group; in which each of R1, R2, R3 and R4 can be the same or different; and

X<sup>-</sup> is defined as an acceptable counter ion.

5

Illustrative counter ions include those associated with clay minerals and may also include but are not limited to fluoride, chloride, bromide, iodide, acetate, carboxylate, ect.

10 As used herein, the term alkyl unless otherwise modified refers to both cyclic and noncyclic groups, although cyclic groups will comprise at least three carbon ring atoms. Alicyclic alkyl groups are generally preferred. Alkenyl and alkynyl groups of compounds of the invention have one or more unsaturated linkages, typically 1 to about 3 or 4 unsaturated linkages. Also, the terms alkenyl and alkynyl as used herein  
15 refer to both cyclic and noncyclic groups, although straight or branched noncyclic groups are generally more preferred. Alkoxy groups of compounds of the invention have one or more oxygen linkages, typically 1 to about 5 or 6 oxygen linkages. Alkylthio groups of compounds of the invention have one or more thioether linkages, typically 1 to about 5 or 6 thioether linkages. Alkylsulfinyl groups of compound of  
20 the invention have one or more sulfinyl (SO) linkages, typically 1 to about 5 or 6 sulfinyl linkages. Alkylsulfonyl groups of compounds of the invention have one or more sulfonyl (SO<sub>2</sub>) linkages, typically 1 to about 5 or 6 sulfonyl linkages. Preferred alkylamino groups of compounds of the invention include those groups having one or more primary, secondary and/or tertiary amine groups, preferably 1 to about 3 or 4  
25 amine groups. Suitable alkanoyl groups have one or more carbonyl groups, typically 1 to about 4 or 5 carbonyl groups. Alkoxy, alkylthio, alkylsulfinyl, alkylsulfonyl, alkanoyl and other groups may be suitably either linear or branched. Carbocyclic aryl as used herein refers to non-hetero aromatic groups that have 1 to 3 separate or fused rings and 6 to about 18 carbon ring members and may include e.g. phenyl, naphthyl, biphenyl, acenaphthyl, phenanthracyl, and the like. Phenyl is often preferred. Suitable  
30 heteroaromatic or heteroaryl groups will have 1 to 3 rings, 3 to 8 ring members in each ring and from 1 to about 3 hetero atoms (N, O or S). Specifically suitable

heteroaromatic or heteroaryl groups include e.g. coumarinyl, quinolinyl, pyridyl, pyrazinyl, pyrimidinyl, furyl, pyrrolyl, thienyl, thiazolyl, oxazolyl, imidazolyl, indolyl, benzofuranyl, and benzothiazol.

- 5 As discussed above, many groups including alkyl groups are optionally substituted. Suitable groups that may be present on a "substituted" substituent include e.g. halogen such as fluoro, chloro, bromo and iodo; cyano; hydroxyl; nitro; azido; sulfhydryl; alkanoyl e.g. C<sub>1-6</sub> alkanoyl group such as acetyl and the like; carboxamido; alkyl groups including those groups having 1 to about 12 carbon atoms, preferably  
10 from 1 to about 6 carbon atoms; alkenyl and alkynyl groups including groups having one or more unsaturated linkages and from 2 to about 12 carbon atoms, preferably from 2 to about 6 carbon atoms; alkoxy groups having one or more oxygen linkages and from 1 to about 12 carbon atoms, preferably 1 to about 6 carbon atoms; aryloxy such as phenoxy; alkylthio groups including those moieties having one or more  
15 thioether linkages and from 1 to about 12 carbon atoms, preferably from 1 to about 6 carbon atoms; alkylsulfinyl groups including those moieties having one or more sulfinyl linkages and from 1 to about 12 carbon atoms, preferably from 1 to about 6 carbon atoms; alkylsulfonyl groups including those moieties having one or more sulfonyl linkages and from 1 to about 12 carbon atoms, preferably from 1 to about 6  
20 carbon atoms; aminoalkyl groups such as groups having one or more N atoms and from 1 to about 12 carbon atoms, preferably from 1 to about 6 carbon atoms; carbocyclic aryl having 6 or more carbons, particularly phenyl; aryloxy such as phenoxy; aralkyl having 1 to 3 separate or fused rings and from 6 to about 18 carbon ring atoms, with benzyl being a preferred group; aralkoxy having 1 to 3 separate or  
25 fused rings and from 6 to about 18 carbon ring atoms, with O-benzyl being a preferred group; or a heteroaromatic or heteroalicyclic group having 1 to 3 separate or fused rings with 3 to about 8 members per ring and one or more N, O or S atoms, e.g. coumarinyl, quinolinyl, pyridyl, pyrazinyl, pyrimidinyl, furyl, pyrrolyl, thienyl, thiazolyl, oxazolyl, imidazolyl, indolyl, benzofuranyl, benzothiazolyl,  
30 tetrahydrofuranyl, tetrahydropyranyl, piperidinyl, morpholino and pyrrolidinyl. A "substituted" substituent of a phosphonium compound of the invention may be

substituted at one or more available positions, typically 1, 2 or 3 positions, by one or more suitable groups such as those listed immediately above.

By the term "salt" is meant that the subject molecule includes one or more ionic bonds. Exemplary salts are onium salts and such as sulfonium, phosphonium and ammonium salts disclosed herein.

In one embodiment of the invention, the inorganic layered silicate has the phosphonium salt represented above in Formula II preferably non-covalently bound thereto. In another embodiment, the invention provides a nanocomposite that includes at least one of the inorganic silicate compounds that have that phosphonium salt. A preferred phosphonium salt is the compound represented by Formula II in which M is P and each of R1, R2, R3 and R4 is independently an octyl or phenyl group the same or different. In another embodiment of the silicate, each of R1, R2 and R3 is a substituted or unsubstituted phenyl group and R4 is a substituted or unsubstituted alkyl group having between from about 16 to about 20 carbon atoms. In a particular embodiment, each of R1, R2 and R3 is a butyl and R4 is a substituted or unsubstituted alkyl group having about 16 carbon atoms. In an additionally preferred embodiment, M is P and the P atom is fully substituted by substituted or unsubstituted phenyl groups, preferably unsubstituted.

In a preferred example of the invention, the inorganic silicate is montmorillonite which includes an underexchanged or overexchanged tetraphenyl phosphonium salt.

In addition to the foregoing ORMLAS, additionally preferred ORMLAS have a preferred d-spacing between layers of from between about 10 to about 60 Angstroms as determined by XRD, preferably from between about 10 to about 50 Angstroms. Typically, the XRD test is performed prior to contact with a desired polymer material. More preferred ORMLAS have a d-spacing of from between about 15 to about 30 Angstroms with about 18 to about 24 Angstroms being preferred for many applications.

Additionally preferred ORMLAS are made from what is sometimes referred to as a "sol-gel" process. The ORMLAS themselves are preferably made from at least one metal alkyl silsesquioxane and especially an alumino-alkylsilsesquioxane. As discussed, the silsesquioxane can be readily modified to make product with desired performance characteristics including substituting the alkyl group with a non-aliphatic group, e.g., alkoxy and/or hydroxy. More preferred ORMLAS exhibit good high temperature stability.

See Example 1-2 below for more detailed disclosure relating to making and using ORMLAS.

Also preferred are ORMLAS of this invention that can be combined with one or a combination of suitable polymer materials including the particular polymers, polymer blends and polymer alloys referenced above. Of particular interest for many applications is a nanocomposite that includes at least one ORMLAS and optionally at least one of the inorganic layered silicates disclosed herein in which the silicate includes a Hytrel polymer intercalated therein. Alternatively, the Hytrel polymer is exfoliated in layers of the ORMLAS. As discussed, preferred Hytrel polymers include Hytrel 5526, Hytrel 5612, Hytrel 4056, Hytrel 5526, and Hytrel 5612.

Preferred use of the foregoing Hytrel nanocomposite includes use in the manufactured articles discussed herein including the claims below.

In embodiments in which the nanocomposite includes at least one ORMLAS, the amount of any particular ORMLAS in the matrix will generally follow the amounts already mentioned for the inorganic layered silicate unless otherwise stated. A preferred compatibilizing agent for use in the ORMLAS is an organo-silane including including molecular and polymeric agents suited for the intended use.

Additionally preferred nanocomposites exhibit good barrier properties as determined by recognized testing procedures and particularly standard solute

transmission rate tests. See generally the American Society For Testing and Materials (ASTM) 1916 Race St. Philadelphia, PA 19103. See also U.S. Pat. No. 5,042,176 to Rudy; the disclosure of which is hereby incorporated by reference. In one embodiment, the nanocomposite includes one ORMLAS or one inorganic layered  
5 silicate combined with a polymer material Hytrel, PET or polypropylene.

Additional transmission rate tests include those used in the field to measure gas transmission rates such as oxygen, nitrogen, carbon dioxide, water vapor, a noble gas; or a mixture thereof. Reference herein to a "standard water vapor transmission  
10 rate test" is meant that test described in ASTM publication D-3985-81 (Reapproved 1988) and entitled "Standard Test Method For Oxygen Gas Transmission Rate Through Plastic Film And Sheeting Using A Coulometric Sensor". Reference herein to a "standard oxygen gas transmission rate test" is meant that test described in ASTM publication F-1249-90 and entitled "Standard Test Method For Water Vapor  
15 Transmission Rate Through Plastic Film And Sheeting Using A Modulated Infrared Sensor". See also the oxygen rate transmission system (modulator OX-TRAN® 2/20) described by MOCOM® (7500 Boone Avenue North, Minneapolis, MN 55428). Particular nanocomposites of this invention feature a gas or liquid transmission rate through the nanocomposite that is preferably at least about 1.5 fold lower than the  
20 neat polymer, preferably between from about 10 to about 200 fold less than the neat polymer as determined by the tests.

More particular "high gas barrier" nanocomposites are described in the discussions and examples which follow.

25

Additional nanocomposites in accord with this invention have been prepared by extrusion of synthetic ORMLAS clays and phosphonium exchanged clays with polyetherimide (PEI), nylon, and polycarbonate (PC). In general, there has been excellent dispersion of the ORMLAS within each of these polymers as shown by  
30 XRD and TEM. The phosphonium clays appear to intercalate. However, good exfoliation has not always been achieved. Both of these clays show excellent thermal stability for the temperatures required for the processing of these materials. Many of

these nanocomposites have been subjected to DMA testing. These results display a higher modulus before and after the  $T_g$  of the materials. Those samples prepared for Nylon, despite no apparent improvement in  $T_g$ , show an improved use temperature due to an excellent enhancement in modulus.

5

As discussed, it is an object of this invention to provide novel ORMLAS which optionally include non-aliphatic chemical groups as part of the compatibilizing agent. Use of such agents in accord with the invention has been found to enhance several performance characteristics of resulting nanocomposites including improving  
10 synthesis and optimizing contact with polymer materials. More particular advantages of these compatibilizing agents include rendering the layered silicate somewhat more hydrophilic and enhancing intercalation and exfoliation. Preferred non-aliphatic groups include hydroxyl and alkoxy groups although other significantly hydrophilic groups can be used to suit an intended application.

15

Additionally preferred nanocomposites according to the invention are thermoplastic materials having good performance characteristics. Preferred nanocomposites are moldable into a variety of articles of manufacture, e.g., by conventional shaping processes, such as melt spinning, blow molding, casting,  
20 vacuum molding, sheet molding, injection molding and extruding. Examples of such molded articles are components for technical equipment, apparatus castings, household equipment, sports equipment including athletic footwear and particularly sneakers, tennis shoes and the like, bottles, containers, components for the electrical and electronics industries, car components, circuits, fibers, semi-finished products  
25 which can be shaped by machining and the like. The use of the materials for coating articles by means of powder coating processes is also possible, as is their use as hot-melt adhesives. The molding compositions according to the invention are outstandingly suitable for specific applications of all types since their spectrum of properties can be modified in the desired direction in a plurality of ways.

30

Additionally preferred articles of manufacture will include or consist of these or other equally suitable nanocomposites of this invention. In one embodiment, the



articles will have at least one of the following performance characteristics: 1) an impact resistance of at least about 10% better than the neat polymer; 2) a tensile modulus of at least about 10% better than the neat polymer; 3) a flame resistance of at least about 10% better than the neat polymer; 4) a glass transition temperature ( $T_g$ ) of at least about 10% better than the neat polymer; 5) a melting temperature ( $T_m$ ) of at least about 10% better than the neat polymer; and 6) a heat distortion of at least about 10% better than the neat polymer. Methods for determining these particular performance characteristics are known in the field and are referenced below. Of course, in embodiment in which the article includes a combination of polymer materials such as a blend or alloy, enhanced performance will typically be referenced against the combined polymer material and not the neat polymer.

Preferred nanocomposites will have at least one of the foregoing performance characteristics when compared to neat polymer material.

The compositions of this invention including dispersed platelet particles are especially useful for fabrication of extruded films and film laminates, as for example, films for use in food and/or beverage packaging. Such films can be fabricated using conventional film extrusion techniques. The films are preferably formed to nearly any desired thickness, e.g., from about 10 to about 100 microns, more preferably from about 20 to about 100 microns and most preferably from about 25 to about 75 microns in thickness.

The nanocomposites of this invention can be formed by any suitable process for forming the composite. For example, nearly any nanocomposite of this invention can be conveniently prepared by blending processes of the type described in U.S. Pat. Nos. 4,739,007, 4,810,734, and 5,385,776; the disclosures of which are hereby incorporated by reference.

In one embodiment of the blending processes described, a suitable monomer precursor of a desired polymer is polymerized following or contemporaneous with intercalation or exfolation. Suitable polymerization techniques include condensation

polymerization, anionic polymerization, hydrolytic polymerization and the like. For example, in one such procedure montmorillonite intercalated with diaminobenzene is combined with phthalic anhydride in about a 1:1 molar ratio. The mixture is stirred at about 160°C in NMP for about 16 hours to yield a polyimide. In this illustration of the invention, Platelet particles comprising one or a few layers of montmorillonite are dispersed through the polymer. A related technique can be practiced with the ORMLAS of this invention. Preferred composites, made with the ORMLAS, inorganic layered silicates, or mixtures thereof can be prepared by melt blending process in which the polymer precursor and the silicate are typically sheared in the melt at a temperature equal to or greater than the melting point of at least one of the polymer materials in the mixture until the particulate materials exfoliate and disperse to the desired extent.

Alternatively, solution polymerization techniques such as those disclosed in above and in Example 7 below may be more appropriate for making particular nanocomposites as discussed previously.

As a more specific illustration of an acceptable melt blend process, a suitable polymer material such as Nylon or Ultem is combined with a desired ORMLAS or inorganic layered silicate as provided herein. That mixture is heated to a temperature sufficient to form a polyetherimide melt which is then sheared by a suitable means such as by standard shearing methods are employed by conventional extruder and injection molding implementations. Particularly good shearing action can be achieved by the polymer melt at one end of an extruder (single or double screw) and receiving the sheared polymer at the other end of the extruder. The temperature of the polymer melt, residence time of the melt in the extruder and the design of the extruder (single screw, twin screw, number of flights per unit length, channel depth, flight clearance, mixing zone etc.) are several variables which are known to impact the amount of shear to be applied.

In embodiments in which exfoliation is desired, the melt including the silicate composition and intercalated material may be subjected to shear mixing until the

desired amount of material exfoliates to an acceptable extent. In general, at least about 80% by weight, preferably at least about 85% by weight, more preferably at least about 90% by weight and most preferably at least about 95% by weight of the material delaminate to form fibrils or platelet particles substantially homogeneously dispersed in the polymer matrix.

As will be appreciated by those in this field, any one or all of the aforementioned synthetic variables can be modified to suit an intended use of the silicate composition and particularly to enhance desired performance characteristics.

A silicate composition of this invention including the preferred nanocomposites already discussed may optionally include various components such as additives usually employed with particular polymer materials. These include optional components, e.g., nucleating agents, fillers, impact modifiers, chain extenders, plasticizers, colorants, uv stabilizers, thermal stabilizers, mold release lubricants, antistatic agents, pigments, fire retardants, and the like. Also included for some applications are conventional clay mineral swelling agents.

In a particular example of an acceptable melt blend process, the extruder used is a twin screw extruder preferably including standard conveying elements, kneading elements and mixing/dispersing elements. Preferably, the extruder is pre-heated to a temperature set of between about 99% to about 110% of the melting point of the neat polymer (or the blend or alloy thereof). In preferred production methods of the invention, there is output of blend (admixture) at a temperature of from between about 102% to about 110% of the melting point of the neat polymer (or the blend or alloy thereof). Starve feeding of the extruder is often preferred. Preferred operation of the twin screw extruder involves a maximum or near maximum pressure during kneading and conveyance stages. A preferred conveyance stage in the extruder is about 3 times longer in duration than the kneading time in the extruder. In this embodiment of the method for making the nanocomposites preferred output from the extruder is in the form of at least one of a rod, film, sheet, blow-molded, or extrusion blow-molded forms.

Specifically preferred is a direct melt process discussed below in Examples 4 and 9 below.

5           The following discussion relates to several preferred aspects of the present invention including specific ORMLAS, inorganic layered silicates, nanocomposites and methods for making and using same. The discussion is meant to more particularly point out the invention. It is not intended nor should it be construed as being illustrative of the scope of this invention.

10           Referring to Figure 1A, state-of-the-art compositions are schematically shown. Nanocomposites 1 have silicate layers 3 with alkyl ammonium surfactants 5 on the surface. The first part of the invention, schematically shown in Figure 1B, provides new organic/inorganic nanocomposites structures 11 by substituting high temperature  
15   organic phosphonium cations 15 for the standard compatibilizing agent, viz., alkyl ammonium cations. In the new invention, ion exchange occurs with the more thermally stable organic phosphonium cations, e.g. tetraphenyl phosphonium 15 (Figure 2). That modification enhances the thermal stability of the nanocomposites from the current level of about 100-150°C to approximately 175-200°C or more  
20   without affecting other physical or mechanical properties of the resulting nanocomposites.

          The inventors have synthesized a new class of phenyl phosphine-based arylene  
25   ether structural polymers that offer excellent mechanical and thermo-oxidative properties. Those polymers are somewhat similar in nature to phenyl phosphonium, are qualified for space missions by NASA and are being commercially produced.

          As schematically shown in Figure 1C, the invention also provides the innovative use of organically modified layered aluminosilicates 23 (ORMLAS) that  
30   combine the layered silicates and the organic compatibilizing agent 25 in a single chemical compound 21, rendering the material thermally stable, and highly organophilic. This dual function compound is then miscible with a host of structural

matrix resins such as polyamides (nylon  $T_m$  120°C), polyether imide (Ultem®  $T_g$  215°C), polyimides ( $T_g$  >275°C) and poly arylene ethers ( $T_g$  >225-350°C). These approaches offer processibility through both, solution techniques, as well as solvent-free direct melt intercalation technique. Moreover, since the bonding of the organic group to the inorganic Si atom is through the Si-C bonds, the ORMLAS exhibits excellent thermal stability. Fabricating ORMLAS layered silicates with high temperature structural polymers offers an attractive combination of properties such as high heat distortion temperature, excellent impact resistance and excellent mechanical properties.

The invention provides high use-temperature light-weight polymer/inorganic nanocomposites which have outstanding properties, compared to the state of the art layered silicate nanocomposites that use alkyl ammonium as the surfactant. A database of properties of control specimens is established for nanocomposites made from mixtures of a number of commodity polymers (e.g., Polystyrene Nylon, modified Polyetherimide, Polyethylene oxide) with montmorillonite containing alkyl ammonium-surfactants (through cation-exchange).

Superior polymer/layered silicate nanocomposites are fabricated by using mixtures of polyetherimide (PEI) resins with montmorillonite containing organic phosphonium surfactants, e.g., tetraphenyl phosphonium (TPP) (through cation-exchange), via direct polymer melt intercalation process.

Superior nanocomposites are fabricated by direct polymer melt intercalating organically-modified layered aluminosilicates (ORMLAS) with polyetherimide and thermoplastic polyimide (PI) or polyarylene ether (PAE) resins. The direct bonding of the organic surfactant group to the structural Si atom through an Si-C bond provides a "built in" surfactant with enhanced thermal stability, and also allows for easy tailoring of the organic-inorganic interface through the organic groups.

Interfacial, thermal, mechanical and physical properties of the fabricated nanocomposites are evaluated to optimize the most promising nanocomposites.

The nanocomposites are designed by creating favorable interactions at the polymer-layered silicate interfaces. That is achieved by making the chemistry of the inorganic reinforcement phase more compatible with the organic polymer matrix, i.e.,  
5 by making the layered silicate surfaces organophilic. The normally hydrophilic silicate surfaces are rendered organophilic after ion-exchange reactions of the loosely-held cations in the interlayer spaces of the silicate structure with organic cations.

Polymer-layered silicate nanocomposites have been synthesized for a variety  
10 of commodity polymer systems. Nanocomposites with properties much superior to that of the corresponding unfilled and conventionally-filled polymers are hence obtained. This unique combination of improved properties, easy fabricability, and low-cost, offers tremendous potential for commercial applications of these materials.

The synthetic creation of polymer/inorganic nanocomposites 31, schematically  
15 shown in Figure 3, exploits the ability of the layered inorganic silicates 23 to accommodate polymer 33 chains 35 between the layers 23 creating intercalated hybrids 37. Delaminated hybrids 39 are created by dispersing individual layers 23 in a continuous polymer matrix 41. Figure 3 shows a schematic representation 31 of the  
20 polymer/inorganic nanocomposite structures 37, 39 obtained using the layered silicates 23. Nanocomposites 37 have single polymer chains intercalated between the silicate layers 23. In nanocomposites 39 the host silicate layers 23 are delaminated and dispersed in a continuous polymer matrix 41.

25 That synthetic design also exploits the ion-exchange capacity of these layered-silicates 23 which allows for a fine-tuning of their surface chemistry to create a favorable organic-inorganic interface.

The advantages of the layered silicates in the synthesis of those  
30 nanocomposites arise from their unique crystal structure. Those layered silicate materials are fine-grained and have crystal structures with a "platy" habit. Their structure is common to the family of 2:1 layered- or phyllosilicates, well-known

examples of which are mica and talc. The structure is composed of  $\text{SiO}_4$  tetrahedra fused to edge-shared octahedra of aluminum or magnesium hydroxides. Layer stacking leads to regular Van der Waals gaps between the layers, viz., interlayer or gallery. Isomorphic substitution of cations is common (for example,  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  substituting for  $\text{Si}^{4+}$  in the tetrahedral network). That leads to a net negative charge on the structure, which is generally counter-balanced by cations residing in the interlayer spacing. Those cations are more or less readily exchanged and result in the cation-exchange capacity of the materials.

Those interlayer cations are, for example,  $\text{Na}^+$  or  $\text{K}^+$  in pristine layered silicates. For the synthesis of the polymer/inorganic nanocomposites, an organophilic surface chemistry is desired to create favorable interactions with the organic polymer matrix. Therefore, those inorganic cations are exchanged with various organic cations, e.g., alkyl ammonium cations. The hydrophilic silicate surface is thus rendered organophilic. Those surfactants typically are alkyl ammonium compounds e.g., dimethyl ditallow ammonium bromide. One example is the use of dimethyl ditallow ammonium bromide to cation-exchange with the  $\text{Na}^+$ -montmorillonite — a layered silicate. Such ion-exchanged 'organo'silicate clays are commercially available. Herein lies the opportunity to tailor the interfacial chemistry of those polymer/inorganic nanocomposites through creation of the organic functional groups. The properties of the nanocomposites can be optimized through interfacial surface chemical design.

The synthesis of layered silicate nanocomposites has involved intercalation of a suitable monomer followed by *in situ* polymerization including the melt processes discussed generally above. Alternatively, polymer intercalation is carried out from solution. These techniques limit use in the case of most technologically important polymers, since suitable monomers and compatible polymer-silicate solvent systems are not always available. The spectrum of nanocomposite systems that can be synthesized is considerably broadened by the advent of a more versatile and environmentally-friendly synthetic approach, called direct polymer melt intercalation. In that approach, the polymer and the silicate are mixed, and the mixture is heated

above the softening point of the polymer. That technique allows the synthesis of a much wider range of polymer/inorganic nanocomposites. Polymers with varying degrees of polarity and crystallinity are directly intercalated into organically-modified layered silicates. Example of polymers use direct polymer melt intercalation include  
5 polystyrene, poly(dimethylsiloxane), poly(vinylidene fluoride), poly (ε-caprolactone), and (polyethylene oxide).

Delamination of the silicate layers can also be achieved during nanocomposite synthesis through 'polymer melt intercalation'. An example is the delamination of the  
10 individual silicate layers achieved by suspending ditallow ammonium-exchanged montmorillonite in PDMS (Polydimethylsiloxane) at room temperature and sonicating for 2 minutes.

The nanocomposites provided by this invention can be compared to those  
15 nanocomposites shown in Figure 4. This figure was obtained from Giannelis, E.P. (1996) *Adv. Materials* 8:29-35. See also Kurauchi, T. et al., (1991) *SAE Technical Paper Series*, 910584. As shown in Figure 4, several Nylon-6 properties are enhanced when the polymer is in nanocomposite form. Similar enhancements were observed for many polymer materials when used to make the nanocomposites  
20 provided herein.

In particular, Figure 4 shows that for Nylon-6 the tensile strength and modulus are enhanced without significant loss in impact strength. Loss of impact strength is usually witnessed with such enhancements in the case of conventional filled  
25 polymers. The significant increase in the heat distortion temperature (i.e., 145°C up from 65°C) extends the use-temperature of Nylon to under-the-hood structural components in automobiles. A reduction in water adsorption accompanies the improvements in mechanical properties. These and other features were seen with the nanocomposites of this invention.

30 Considerable increases in heat resistance and thermal stability are obtained with these nanocomposites. Polydimethylsiloxane-layered silicate nanocomposites



have a delayed thermal decomposition compared to that of the pure polymer – which decomposes into volatile cyclic oligomers. The improved barrier properties of these nanocomposite materials are demonstrated through measurements of relative permeability of liquids and gases through the nanocomposites. Dramatic reductions in permeability are obtained at low inorganic contents compared to conventionally-filled polymers with much higher filler contents. The large aspect ratio of the silicate layers forces the solutes to follow more tortuous paths in the polymer matrix around the silicate layers. That results in much larger effective diffusion distances, and hence lower permeabilities. The enhanced thermal stability of the nanocomposites is also attributed to the hindered out-diffusion of the volatile decomposition products. Self-extinguishing characteristics in those materials are related to the barrier properties rendered by the silicate layers.

A key to obtaining superior properties at low inorganic loadings is the homogeneous nanoscale dispersion of the inorganic phase in the polymer, and the creation of favorable interactions at the organic-inorganic interface. Favorable interfacial chemistry leads to organic and inorganic phases being dispersed at a nanometer level. The superior properties of the new composites are obtained at low inorganic loadings. The use of low inorganic contents leads to significant advantages. High degrees of stiffness, strength and barrier properties are obtained with far less inorganic content than comparable glass- or mineral reinforced polymers. Considerable weight savings are, therefore, obtained.

Some commercial applications of these materials are, for example, Nylon-layered nanocomposite automatic timing belt cover. Other applications include airplane interiors, fuel tanks, components in electrical and electronic parts, under-the-hood automotive structural parts, brakes and tires. Applications of nanocomposite barrier films may be used in food packaging and in other applications are also possibilities.

30

The fact that the nanocomposites yield significant enhancements in properties at low inorganic loadings also provides ease-of-manufacturing and several cost-

benefits. It allows for the use of simple manufacturing techniques (viz., extrusion, injection-molding and casting) which are normally used for pure polymers.

Therefore, the nanocomposites can be manufactured at a much lower cost than the more conventional fiber- or mineral-reinforced composites which require more  
5 expensive fabrication procedures. That provides further reasons for their commercial appeal.

Commodity polymers provide use-temperatures below 125°C. Substructure applications for rockets and aircrafts require higher long term use-temperatures of  
10 about 175°C and 250°C.

The thermal stability of the current state-of-the-art nanocomposite systems is often limited by the thermal instability of the surfactants used to create favorable interactions at the interface. Those surfactants typically are alkyl ammonium  
15 compounds. One example is the use of dimethyl ditallow ammonium bromide to ion-exchange with the Na<sup>+</sup>-montmorillonite - a layered clay. The thermal stability of the nanocomposite system is therefore, limited by the thermal stability of the alkyl ammonium compound. Degradation of those surfactant molecules, and hence that of the organic-inorganic interface, begins at temperatures around 100-110°C.

The invention provides more thermally stable surfactants, which optimize the dispersion of the inorganic phase, and also enhance the compatibility at the organic-inorganic interface through the creation of favorable interactions. The invention therefore provides enhanced use-temperatures of the nanocomposites. One part  
25 elevates the use-temperature of the nanocomposite system by using more thermally stable surfactants than the currently used alkyl ammonium compounds.

The first part provides tetra-phenyl phosphonium compounds (with thermal stability in the range of 190-200°C) to carry out a cation-exchange with the layered  
30 silicate reinforcement. Tetraphenyl phosphonium is a reactive salt with a net positive charge, as shown in Fig. 2. The salt readily ion exchanges with the cation on the surface of the inorganic phase attaching itself from the oxide surface and thus

rendering the surface organophilic. That surface modified system lends itself to direct melt intercalation. Because tetraphenyl phosphonium is a high temperature organic moiety with thermal stability in excess of 200°C, the first part of the invention provides nanocomposites which will satisfy the need for long-term use-temperatures of 175°C-200°C.

The second part of the invention extends the use-temperature of the nanocomposites to over 250°C. It is based on the innovative use of organically-modified layered alumino-silicates (ORMLAS) that combine the layered silicate and the organic surfactant/compatibility agent in a single chemical compound. The organic surfactant groups are bonded to the structural Si atom through thermally stable Si-C bonds. The thermal stability of the overall system is therefore greatly enhanced. Therefore, those materials provide unique inorganic layered silicate reinforcements having markedly more thermally-stable surfactants "built-in" to the chemical structure. Those materials are miscible in a host of structural matrix resins, such as polyamides (nylon T<sub>m</sub> 120°C) and polyether imide (Ultem T<sub>g</sub> 215°C), polyimides (T<sub>g</sub> > 275°C) and poly arylene ether (PAE T<sub>m</sub> > 325-350°C).

Those ORMLAS materials are synthesized using the sol-gel process where the organic groups are incorporated into the molecular structure through the use of organically modified silicon alkoxides, i.e., precursors containing Si-CxHx bonds. The organic functionality is therefore directly bonded to the structural Si atom by the Si-C bond. The organically modified aluminosilicate will be synthesized using mixtures of organically-modified silicon alkoxides and solutions of aluminum chloride. The standard approach combines an alcohol solution of aluminum chloride with an alcohol solution of organically functionalized alkoxysilane. The organically functionalized trialkoxysilane, e.g., alkyltriethoxysilane, provides alkyl organic groups connected directly through Si-C bonds. The mixture is then condensed (crosslinked) to form a gel at appropriate pH conditions by the addition of NaOH. The gel is aged, filtered, washed with distilled water, and then dried in vacuum. That procedure yields a stable layered organophilic compound. The resulting material is either precipitated as a powder, dried and ground to appropriate particle size, or case

into various shapes and forms. In that cast, the ORMLAS is precipitated as a powder or ground and classified it into appropriate size particles for incorporation with the polymer matrix for direct melt intercalation. A unique feature of those ORMLAS compounds is that they are especially engineered to delaminate in the presence of a variety of polymer resins - thus promoting the dispersion of the inorganic layers in the polymer matrix. That versatile and innovative new feature yield nanocomposites which will satisfy needs for a range of use-temperatures extending to long-term use-temperatures over 250°C.

10 In addition to the enhanced thermal stability, the use of synthetic organically-modified layered silicates (ORMLAS) having built-in surfactants eliminates the poisonous alkyl ammonium surfactants which limit the applications of nanocomposites as food packaging materials. The elimination of the ion-exchange also lowers the processing costs. Therefore, that technique yields recyclable and more  
15 cost-effective food packaging materials with superior gas-barrier properties to replace unrecyclable multilayer plastic food packaging materials.

The following examples and discussion address particularly preferred embodiments of the chemical optimization of ORMLAS materials, the optimization  
20 of phosphonium exchanged natural clays, the extrusion fabrication of Ultem-nanocomposites using the layered silicates with higher thermal stability, and the analysis of the nanocomposite properties. In particular, the following describe the synthesis of long chain phosphonium exchanged natural clays. A discussion of the fabrication of a variety of nanocomposites using polymers such as Ultem, and Nylon  
25 is additionally provided. As also disclosed below in the examples, the silicate compositions of this invention including the nanocomposites can be characterized by one or a combination of different strategies such as Differential Scanning Calorimetry (DSC), Transmission Electron Microscopy (TEM), Dynamic Mechanical Analysis (DMA), Heat Distortion Temperature (HDT). These and other material  
30 characteristics can be detected and quantified if desired using conventional tests well known in the field. See, e.g., the ASTM.

Unless specifically mentioned otherwise, the phrase "heat distortion temperature" or related term or phrase is meant thermo-mechanical analysis used to determine how the presence of a particular nanophase inorganic affects the heat distortion temperature of the subject, new material. Preferred is the standard test performed by SGS US Testing Company Inc. (Fairfield, NJ).

By the phrase "dynamic mechanical analysis" or related term or phrase is meant a dynamic measurement of the modulus with respect to temperature. As will be understood, this property is an important gauge of the actual use temperature of the material and it provides a measure of the enhancements in use-temperatures of the polymers, e.g., a result of the nanoscale distribution of the inorganic phase.

By the phrase "thermal stability" or related term or phrase is meant stability detectable by differential scanning calorimetry (DSC) and particularly the change in the glass transition temperature of the matrix polymer as well as thermal performance of the resulting nanocomposites.

By the phrase "interfacial characterization" or related term or phrase is meant interface characterization as determined by Transmission Electron Microscopy (TEM). The present disclosure provides many examples of the layered structure of the ORMLAS materials as well as the nanoscale dispersion of the inorganic layers within selected polymer materials. Interfacial properties are often critical for long term rise of the nanocomposites.

By the phrase "tensile properties" or related term or phrase is meant tensile strength, tensile modulus and elongation to break for each polymer system as assessed in accordance with ASTM standards. Preferred is Instron testing.

By the phrase "impact resistance" or related term or phrase is meant ASTM standard for impact resistance and particularly to assess the nanocomposite impact strength. Nanocomposite pellets will be used to mold appropriate articles to accommodate this testing.

By the term "dispersion of inorganic phase" is meant wide angle x-ray diffraction (WAXD) pattern of the nanocomposite to generate data to evaluate the orientation of the inorganic phase within the polymer matrix. This disclosure provides powder XRD patterns to obtain information about the extent of dispersion of the silicate layers in the polymer.

"Layered material" shall mean an inorganic material, such as a smectite clay mineral, that is in the form of a plurality of adjacent, bound layers and has a thickness, for each layer, as specified herein.

"Platelets" shall mean individual layers of the layered material.

"Intercalate" or "Intercalated" shall mean a layered material that includes polymer material disposed between adjacent platelets of the layered material. In most instances, the word "intercalate" or "intercalated" shall also mean an increase in interlayer spacing between the adjacent platelets by at least about 2 Å.

"Intercalation" shall mean a process for forming an intercalate.

"Intercalant polymer" or "intercalant" shall mean an oligomer or polymer that is sorbed between platelets of the layered material and complexes with the platelet surfaces to form an intercalate.

"Intercalating carrier" shall mean a carrier comprising water with or without an organic solvent used together with an intercalant polymer to form an Intercalating Composition capable of achieving Intercalation of the layered material.

"Intercalating pomposition" shall mean a composition comprising an intercalant polymer, an intercalating carrier for the intercalant polymer, and a layered material.

"Exfoliate" or "exfoliated" shall mean individual platelets of an intercalated layered material so that adjacent platelets of the intercalated layered material can be dispersed individually throughout a matrix polymer; or throughout a carrier material, such as water, an alcohol or glycol, or any other organic solvent.

5

"Exfoliation" shall mean a process for forming an exfoliate from an intercalate.

10 "Nanocomposite" shall mean an oligomer, polymer or copolymer having dispersed therein a plurality of individual platelets obtained from an exfoliated, intercalated layered material.

"Matrix polymer" shall mean a thermoplastic or thermosetting polymer in which the Intercalate and/or exfoliate is dispersed to form a nanocomposite.

15

As discussed, the invention features nanocomposites that have good barrier properties particularly to at least one solute such as a gas or liquid. Preferably, the nanocomposites exhibit a significant barrier to gas such as water vapor.

20 U.S. Provisional Application U.S.S.N 60/139,481 entitled "Nanomaterials for Barrier Applications" and filed on June 17, 1999 provides a variety of nanocomposites and methods for making same; the disclosure of which is hereby incorporated by reference.

25 In particular, the U.S.S.N 60/139,481 application discloses layered organo alumino silicate fillers and methodology for producing a variety of layered alumino-silicate nanomaterial filled polymers. Preferred methods include thermoplastic processing techniques to produce high performance nanocomposite layer silicate-filled thermoplastic polymers. The approach is based on the use of  
30 layered silicates with organofunctional groups examples of which are described herein. Also provided are alkyl ammonium montmorillonite layered aluminosilicates as additives to a host of polymer materials and particularly thermoplastic polymers.

Examples of polymers include polyolefins, polyesters, copolyesters, polyurethane and polyurethane copolyester copolymers. Preferred organofunctionalized silicates contain organic contents varying from 20 percent up to 65 percent by weight. The organosilicates can be added in quantities less than 1 percent up to 22 percent by weight.

A preferred method of processing the nanocomposites disclosed in the U.S.S.N 60/139,481 provisional application is by thermoplastic compounding. Single or twin screw extruders are used as the preferred processing equipment. The nanocomposite organosilicate additive can be incorporated simultaneously with the polymer matrix by premixing the filler powder with polymer pellets, granules or powder.

The polymer/nanocomposite material preferably is produced by first introducing the polymer resin into an extruder. Applying heat melts the polymer. The layered silicate additive is introduced to the molten polymer, by the same or a separate port. The two-step process enhances the mixing action associated with nanocomposite and leads to better performing nanocomposites. In this invention nanocomposites and nanomaterials refers to the resultant polymer combined with the layered organoaluminosilicates (nanocomposite fillers) which provide enhanced barrier qualities.

As discussed in the U.S.S.N 60/139,481 provisional application, nanocomposites produced using alkyl ammonium montmorillonite layered aluminosilicates with Hytrel 5526 or Hytrel 5612 at contents varying from 5% up to 12.5%, and preferably about 7.5%, by weight of the layered aluminosilicates. The extruded products resulted in excellent resistance to gas permeation as well as unexpected enhancement in mechanical and physical properties. Hytrel is a du Pont trademark that refers to particular thermoplastic extrudable and blow moldable low modulus of elasticity polyester elastomer resin. Hytrel is a butylene/poly (alkylene ether) phthalate plus stabilizer. The first two numbers refer to hardness on the



Rockwell hardness R scale. The third number refers to inherent viscosity and flowability. The last number refers to the type of antioxidant contained.

Blow molding experiments have demonstrated the blow moldability of Hytrel 4056, 5526 and 5612 nanocomposites. However, the work has also pointed out difficulty in cutting the extrudate using a "hot-knife." The problem appears to relate to the extrudate sticking to the knife. This problem has not been noticed with neat Hytrel 5612 resin. The selection of 5526 grade was based on its excellent impact resistance and low melt flow viscosity, compared to 5612. The addition of layered silicates to 5612 makes it easier to process that thick grade of Hytrel. Hytrel 5612 is a blow molding grade that has been successfully blow molded. Hytrel 5556 is a high impact strength grade with flow viscosity between the 5612 and 5526 grades.

As disclosed in the U.S.S.N. 60/139,481 provisional application, all three grades of Hytrel are compounded with layered silicates to carry out blow molding experiments. A preferred compounding method is provided as follows.

The components are combined by adding the powder into the molten material and mixing and shearing in a screw extruder, using a high screw rpm (above about 130 and preferably about 150 to 167 or up to about 1000 rpm) to decrease residence time, increase yield, and conserve energy. All of these parameters are of interest.

The new layered silicate nanocomposite elastomeric compounds are effective barrier materials.

25

The invention disclosed in the U.S.S.N 60/139,481 provisional application provides new nanotechnology and is well-suited for a wide spectrum of uses including use as a gas encapsulation medium. In particular, the invention is focused on identifying suitable elastomeric resins that are reinforced with nanolayered aluminosilicate inorganic materials at loading levels from below about 5 percent by volume to above about 22% by volume. Emphasis is placed on defining the optimum inorganic reinforcement that maximizes the barrier properties of the base resin with

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minimum adverse effect on the processability, toughness and fatigue properties of the resin.

Having identified the most suitable organic/inorganic nanostructures, the invention further involves fabrication and demonstration of uses of the most successful nanostructure systems and prototype pouches.

In particular embodiments of the invention disclosed in the U.S.S.N. 60/139,481 provisional application, three matrix resins are reinforced at 5% by volume with two specialty nanolayered aluminosilicates each. The matrix resins are three.

- (1) Polyurethane, the current material used in pouches, is used as a baseline material.
- (2) Hytrel 4056 is a du Pont low modulus, extrusion grade thermoplastic polyester elastomer resin with wide industrial usage. Hytrel is a butylene/poly (alkylene ether) phthalate plus stabilizer.
- (3) Hytrel/PET Blend is partially crystalline thermoplastic elastomeric compound that combines processability with enhanced barrier properties used as a component in blends. PET is polyethylene terephthalate to which may be added fillers, and which may be modified with other additives such as plasticizers, lubricants, antioxidants and pigments.

The Hytrel 5526 is in granular or powder form. The other Hytrel materials are pellets. All are dried before melting. The nanocomposite fillers are fine granular powders that do not require drying. After drying the base components Hytrel or Hytrel/PET blend are melted at above 235°C and above 255°C, respectively, and are sheared in a screw conveyor. The melt temperature is maintained, and the nanocomposite additive powder is added. Shearing and mixing continue. Applied heat may be dropped as the shearing continues the input of heat to maintain the melt temperature. The materials are thoroughly mixed before being forced through a film extrusion die.

Layered aluminosilicate reinforcements offer maximum compatibility with the resins of choice and minimize departure from standard processing conditions of the neat resins. The table shown immediately below presents a test matrix.

5

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<b>Proposed Experimental Matrix</b>				
		<b>Polyurethane</b>	<b>Hytrel 4056</b>	<b>Hytrel PET</b>
	<b>Blend</b>			
5	Neat Resin Systems	0 Vol%	0 Vol%	0 Vol%
	Layered	5 Vol%	5 Vol%	5 Vol%
	Aluminosilicate A			
	Layered	5 Vol%	5 Vol%	5 Vol%
	Aluminosilicate B			

10

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Other runs were performed using Hytrel 5526 and 5612 with loadings of about 5%, 10% and 7.5% by weight nanocomposite aluminosilicates A and then B.

5 Neat and nano-reinforced resin systems are used in a thermoplastic extrusion process to produce ASTM compliant flat 2.0 in x 2.0 in specimens at from about 0.030 to about 0.060 (0.75 to 1.5 mm) in thickness. Duplicate gas transmission rate information for helium and nitrogen are generated. The performance of the resulting nanocomposite structures are compared with that of polyurethane pressurized pouch  
10 currently used in footwear applications. Nanocomposite specimens and the gas transmission test results show improved performance over the basic resins.

The nanocomposite system(s) identified above are scaled up and blow molded into pouches. These pouches are inflated with gaseous form of helium with a  
15 secondary nitrogen gas.

The resulting pouches undergo evaluation including barrier, life cycle fatigue, puncture resistance and crazing.

20 Hytrel is a blow moldable composition. The first two numbers in the designations designate hardness, and the third number designates flowability, the lower numbers having higher viscosity and lower flowability. Most of the Hytrel compositions are supplied in pellets. Preferably before molding the Hytrel is dried overnight (about 8 hours) at about 71°C. Before molding the Hytrel is dried at about  
25 99°C for about 3 hours. The layered aluminosilicates need no drying. They may be added to the Hytrel during the drying, when they are mixed with the Hytrel before melting. However, it is preferable to melt and shear the Hytrel and then add the layered nanocomposite fillers. The Hytrel has a melting point of about 170°C to about 220°C (about 338°F to about 428°F). There are no volatiles and no gases to be  
30 removed upon melting.

The PET in the Hytrel/PET blend enhances the entire blend with the increased strength of PET and has a melting point of about 250°C to 255°C (about 482°F to 491°F). The PET has a slightly higher specific gravity, about 1.55 to about 1.81, than the Hytrel, about 1.14 to about 1.27.

5

Anti-sticking additives in the form of antioxidants or antiblocking agents, such as Kemamide B (Hunko Sheffield Chemical Division, P.O. Box 398, Memphis, TN, USA) and Crodamide SR (Croda Universal Limited, North Humberside, DN14 9AA, England), may be added if desired.

10

The U.S.S.N 60/139,481 provisional application discloses particular methods of making nanocomposites having Hytrel or Hytrel/PET blends.

For example, granular or pelletized thermo polymer is melted in a first stage of a twin screw extruder, where the temperature is kept above the melting point of the Hytrel or Hytrel/PET blend. When the Hytrel is molten and is sheared by the screw flights, the nanocomposite powders are added. That may be up to about halfway through the screw extruder. Pitches and diameters are increased and varied following the addition of the nanocomposite additives to thoroughly mix and shear the components, while the temperatures within the components are held above the melting temperatures.

Preferably 1000 rpm speeds are maintained on drive motors. The extruder screw gear ratio may be about 6:1 or 3:1. Therefore actual screw speed at 1000 rpm may be about 167 rpm or 333 rpm. Temperatures are maintained throughout the screw conveyor to about 235°C in the case of Hytrel, and about 265°C in the case of the Hytrel/PET blend, to sustain a high throughput. Applied temperatures in latter zones are adjusted slightly downwardly, as screw pitches and shear changes keep melt temperatures above the desired levels.

30

In examples, Hytrel is fed to screw extruders at rates of from about 65 to about 113 kilograms per hour. Nanocomposite fillers are fed from about 7 to about 13

kilograms per hour. Total feed rates are about 75 to about 125 kilograms per hour. Dwell time in the screw extruder is about 6 to 10 minutes. Extruders used in the examples had a one inch size with a length diameter ratio of 24:1, and were used without event. A three horsepower motor drove the extruders. The extruders had a  
5 breaker plate and screens of 40 mesh and were operated at a pressure of about 450 psi. The melt was cooled to about the melt temperature at extrusion. Automatic air cooling followed by water cooling of the extruded sheets was used. Screws had thread depths of from about 0.180 inches to about 0.060 inches. In one example, extruders had eight feed flights, eight transition flights and eight metering flights. The material was  
10 extruded through an eight inch sheet die at a 30 mil thickness. The material was collected on a three-roll sheet stack and winder and was auxiliary water cooled. The thickness of the sheet may be varied from about 30 mils to about 60 mils, and the width of the sheet may be about 6 to 8 or 7.75 inches.

15 The preferred organoaluminosilicate powder additives are polymer/inorganic nanocomposite materials with enhanced thermal stability and performance characteristics developed by Triton Systems. Two techniques enhance the thermal stability of the nanocomposite systems to over 250 °C. The two unique approaches are based on innovative chemical design of the organic-inorganic interface using (i) more  
20 thermally stable surfactants/compatibility agents, and (ii) more thermally stable synthetic organically-modified layered-silicate reinforcements to create unique nanocomposites. These approaches offer processibility through both solution techniques, as well as solvent-free direct melt intercalation technique.

25 Synthetic organically-modified layered silicates having built-in surfactants are used, as well as alkyl ammonium surfactants.

The properties of these nanocomposites are optimized in order to manufacture these materials in commercially applicable forms, e.g. films, fibers and molded  
30 components. The new technology provides hitherto unobtainable thermal stability and performance characteristics, and has numerous applications in automotive, aerospace, electronic and food and beverage industries.

Reference herein to "high gas-barrier" nanocomposite or a related term is meant that the nanocomposite is capable of retarding the transmission rate of a gas solute through a nanocomposite (or blend thereof) by at least about 1.5 fold lower than the neat polymer, preferably between from about 10 to about 200 fold lower than the neat polymer as determined by standard tests described previously including the oxygen and water vapor transmission rate tests.

In some embodiments, it will be helpful to express reduced diffusion of solute through a particular nanocomposite in terms of transmission rate of a gas such as air, oxygen, water vapor or a noble gas, e.g., helium. Examples of such high gas-barrier nanocomposites include those in which Hytrel, PET or polypropylene or a blend or alloy thereof; is the preferred polymer material. More preferred are nanocomposites formulated into a manufactured article such as a cushioning or gas bladder structure and exhibiting a helium transmission rate of less than about  $20 \times 10^{-8}$  cm.cm<sup>3</sup>/sec.cm<sup>2</sup>.atm.

Additionally preferred high-gas barrier nanocomposites in accord with this invention are made from at least one suitable layered silicate material and at least one suitable polymer material as printed herein. In many instances, a desired high gas-barrier nanocomposite will include one layered silicate and one suitable polymer although other combinations may be more suited for specific applications. In a particular embodiment, the nanocomposite will include between from about 0.5% to about 10% by weight of the layered silicate, preferably about 1% to about 8% of the layered silicate, with about 5% by weight being preferred for many applications.

Illustrative layered silicates and polymer materials for making the high gas-barrier nanocomposites include those which can be readily compounded at about 250°C. Preferred corresponding strategies include using recognized "in line" thermoforming steps. Preferred layered silicates include naturally occurring Na<sup>+</sup>-Montmorillonite ion-exchanged with (i) Dimethyl hydrogenated-tallow (2-ethyl hexyl) ammonium compounds, and (ii) Methyl tallow bis(2-hydroxyethyl ammonium



compounds. Methods for conducting the ion-exchange are provided below. Preferred polymer materials include PET, polyolefin, EVOH, as well as other suitable materials.

5 As discussed in the following Examples, one method of making the high gas-barrier nanocomposites involves positioning at least one and usually a plurality of high aspect ratio silicate layers within a selected polymer material including blends or alloys thereof. A particular high gas-barrier nanocomposite is shown schematically in Figure 23.

10

The high gas-barrier nanocomposite shown in Figure 23 can be made by one or a combination synthetic routes. Particular routes generally achieve good nano-dispersion of silicate layers within the polymer material. A more particular synthetic route involves optimizing silicate platelet dispersal within the polymer matrix on or about a nanometer scale.

15

The high-gas barrier nanocomposites of this invention preferably include silicate layers with high aspect ratios. This feature of the invention provides several advantages. For example, the large aspect ratio typically forces gaseous solutes such as air, oxygen or water vapor, to follow more tortuous paths within the polymer matrix and around the silicate layers when compared to a neat polymer control. The resulting high gas-barrier nanocomposite possesses a larger effective diffusion distance and lower solute permeability when compared to conventional nanocomposites. The arrow in Figure 23 exemplifies the lowered solute permeability.

20 Also, the nanocomposites usually require small amounts of the layered silicate phase (e.g. about 5% by wt) to achieve good high gas-barrier properties. This characteristic of the invention provides several particular benefits including reducing the amount of precursor needed to make the nanocomposites and facilitating processing steps, e.g., by improving contact between the silicate layers and excess polymer material.

30

In contrast to the high gas-barrier nanocomposites of this invention, conventional filled-polymers generally require much more of the silicate phase.

Accordingly, those polymers cannot easily provide the advantages offered by these nanocomposites.

As discussed, the invention encompasses a wide spectrum of manufactured articles. One such article is adapted to hold one or more compositions such as a pharmaceutical or drug composition. Preferred are those compositions having a solid dosage form, e.g., pill, tablet, capsule and the like. An illustrative use of the article is in combination with at least one sheet or strip assembly such as those routinely used to retain pharmaceuticals for storage, shipping and the like. More particular assemblies include foil and/or paper based assemblies that can be adapted in sealing disposition with the article. In this embodiment of the invention, the combination of the article and the sheet or strip assembly will often referred to as a "blister" or "bubble" pack or related phrase.

In another embodiment, the article can be adapted to essentially completely hold the composition without combination with the sheet or strip assembly. This example of the invention has many applications including use in situations where long-term or highly protected storage of the composition is desirable.

The invention contemplates a wide variety of more specific articles including the blister pack. In one embodiment, the article is formulated to include at least one of the disclosed nanocomposites which nanocomposite will preferably includes at least one of the polymer materials disclosed herein. In this embodiment, the nanocomposite will include at least one of the inorganic layered silicates provided herein (e.g., ORMLAS) and at least one of the disclosed polymer materials. Choice of a particular nanocomposite (or blend thereof) for use with the article will be guided by understood parameters such the performance characteristics needed for a particular application including strength and impact resistance. In many instances, the high barrier properties of the articles will be of specific interest.

In particular, in embodiments in which the article is intended for use as the blister pack, articles exhibiting high barrier properties will often be preferred. Choice

- of a particular nanocomposite (or blend of nanocomposites) for making the article will be guided by pre-determined capacity of the nanocomposite to exclude at least one solute such as gas (e.g., air, oxygen or water vapor). Preferred capacity will positively impact the usefulness of the article e.g., by enhancing the shelflife and/or storage characteristics of the composition to be held and protected by the article.
- 5

- In a more specific embodiment, the article will include and usually consist of a nanocomposite that features a gas transmission rate that is preferably at least about 1.5 fold less than the neat polymer, preferably at between from about 10 to about 200 fold less than the neat polymer and as determined by standard transmission rate tests. Specifically preferred tests include those formatted to measure oxygen and water vapor transmission rates through the nanocomposite (or article) as discussed previously.
- 10

- As discussed, the invention also features polyolefin-layered silicate polymer nanocomposite materials. In one embodiment, the materials include polyolefin, comprising between from about 40 to about 99% by weight of nanocomposite; polyamide, comprising between from about 1 to 55% by weight of polyolefin; what is referred to herein as "functionalized grafted polyolefin" comprising between from about 0.5 to about 25% by weight of polyamide polymer; organoclay, comprising between from about 1 to about 40% by weight of the polyolefin; and, optionally, synthetically formulated organoclay formed by self-assembly techniques, comprising between from about 0 to about 25% by weight of the polyolefin.
- 15
- 20

- The foregoing polyolefin-layered silicate polymer nanocomposite materials can be made from a variety of specific components.
- 25

- For example, in one embodiment, the polyolefin is polypropylene or polyethylene. A particular polyamide is Nylon 6, Nylon 66 or Nylon 12 and a particular functionalized grafted polyolefins is a homo- or copolymer of polyolefin with maleic anhydride and/or methacrylic acid grafting functionality, or maleic anhydride and/or epoxy grafting functionality.
- 30

In addition, the polyolefin-layered silicate polymer nanocomposite materials can be made from one or a combination of clay minerals. As an illustration, a preferred organoclay is 2:1 layer phyllosilicate (smectite), or mixed layer silicates (smectite-illite, smectitechlorite, smectite-kaolinite) where exchangeable interlayer cations (K, Ca, Mg, Na, Li, Cu, Al) are completely or partially substituted by organocations, including but not limited to functionalized or non-functionalized alkyl ( $C_8$  to  $C_{24}$ ) - ammonium ions [from  $C_8H_{17}H_3N^+$  to  $C_{24}H_{49}N^+$ ] or alkyl ( $C_8$ -  $C_{24}$ ) -trimethylammonium ions [from  $C_8H_{17}N^+(CH_3)_3$  to  $C_{24}H_{49}N^+(CH_3)_3$ ] or aliphatic amino acids [from  $C_8H_{17}COOH$  to  $C_{24}H_{49}COOH$ ]. If desired, interlayer organocations may contain alkylene (alkyl-phenyl) groups. Preferably, the periodicity of organoclay is from 1.8 to 10 nm in order to provide intercalation of polymers in interlayer spaces of the organo-layered silicates and/or delamination of individual layers of the silicate particles with further exfoliation of those layers within polymer or polymer blend matrix during processing.

Preferred synthetically-designed organo-clays are organically-modified layered aluminosilicates that combine the layered silicate and the organic surfactant and the organic surfactant in a single chemical compound. The organic surfactant groups are bonded to the structural Si atoms through Si-C bonds. These materials provide unique inorganic layered silicate reinforcements with stable organic surfactants "built-in" to the chemical structure. A unique feature of these compounds is that they are especially engineered to delaminate in the presence of a variety of polymer resins including polyolefins and polyamides, and therefore display excellent dispersion of the individual layers in the polymer matrix.

The polyolefin-layered silicate polymer nanocomposite materials of this invention (sometimes referred to as "polymer alloy nanocomposites") provide important advantages.

For example, in embodiments in which the organoclay is intercalated, delaminated or exfoliated, there is provided a significant improvement in gas/moisture

barrier properties of material. Also, when a compatibilizing grafting polymer is employed it desirably provides for grafting of polyolefin to the surface of polyamides. This feature of the invention has advantages including making homogeneous polymer blend with strong bonds in between phases.

5

The polyolefin-layered silicate polymer nanocomposite material can be made by one or a combination of different strategies including the methods disclosed herein or related methods. As an example, the material can be prepared by non-solvent-based melt-processing method in an extruder at the range of temperatures from at least about 190°C, preferably from between about 190°C to about 260°C. The compounding provides sufficient homogenization, shearing, and mixing of ingredients without noticeable molecular weight degradation of polymer-blend components.

As mentioned, the polyolefin-layered silicate polymer nanocomposite materials provide advantages including displaying superior mechanical as well as gas-barrier properties. Without wishing to be bound to theory, it is believed that presence of the high aspect ratio barrier layers in the path of the diffusing gas leads to much larger effective diffusion distances for the gas species (e. g., oxygen, water vapor), and creates nanocomposites with excellent gas-barrier properties. Improvements in tensile strength, mechanical durability, impact resistance, abrasion resistance are also obtained as a result of forming nanocomposites from the neat polyolefin. Additional advantages of preferred materials include unprecedented impact resistance; exceptional gas and moisture barrier; maintenance of reasonable optical transparency; thermoformability via techniques such as injection molding and sheet extrusion; recyclability.

See Example 12 below regarding more preferred polyolefin-layered silicate polymer nanocomposite materials

The following examples are provided to point out preferred aspects of the invention and are not intended to be indicative of the scope of the invention.

### Example 1- ORMLAS Syntheses

The ORMLAS synthetic layered silicates were prepared by our standard self-assembly route by the titration of  $\text{AlCl}_3$  and the organotrialkoxysilane in EtOH with NaOH.

5

Three ORMLAS were prepared by the following standard route by the titration of  $\text{AlCl}_3$  and the organotrialkoxysilane in ethanol with NaOH. The XRD patterns for the alumino- octyl, dodecyl, and octadecyl silsesquioxanes are shown in Figures 5, 6, and 7, respectively. The patterns clearly show an increase in d-spacing (25.1, 37.5, 53.5 Å respectively), as well as improved crystallinity, as the organic chain length is increased. Thermal analyses as described below showed the effect of chain length on the thermal stability of these materials. Previous TGA experiments on the dodecyl analogue have shown that the layered structure is intact up to temperatures of 350 °C in either air or inert atmosphere. An increase in organic chain length is likely to lead to a better dispersion of the silicate layers, and to a more delaminated nanocomposite. The increase in hydrophobicity will also yield better interactions with hydrophobic polymers.

15

A particular goal of these studies was to increase the aspect ratio of the layered silicates by increasing the length of the individual silicate layers of the ORMLAS materials. Impact on the effect of plate size (aspect ratio) on gas barrier and thermo-mechanical properties of the nanocomposites can also be addressed.

20

A preferred method of making the ORMLAS was as follows: An aqueous solution of NaOH (0.1M) was added dropwise with vigorous stirring to  $\text{AlCl}_3$  (6.04g, 25mmol) and dodecyltriethoxy silane (16.63g, 50mmol) in ethanol (250ml) to a pH of 5.5 at room temperature. A white precipitate that formed was allowed to age in solution for 16 hours. Then the solid was filtered, washed with water, and dried at 90°C for 6 hours.

25

30

More particular details about the mixed ORMLAS synthesis is as follows:

The synthesis for the mixed ORMLAS materials was the same as that for the standard ORMLAS except that a mixture of the organosilanes were added. For example, for a ORMLAS material with a 1:1 ratio of methyl:dodecyl, a 1:1 molar ratio of methyltriethoxysilane and dodecyltriethoxy silane were used in the synthesis.

For additional disclosure relating to making the ORMLAS see Ukrainczyk, L. et al. Materials Research Society Symposium on *Nanocomposites of Layered and Mesoporous Materials*, Boston, MA, December, 1996; Fukushima, Y. and M. Tani, *J. Chem. Soc. Chem. Commun.* pg. 241 (1995); and Ukrainczyk, et al. *J. Phys. Chem. B.* 101: 531 (1997).

As discussed, Alumino n-Dodecylsilsesquioxane, Alumino n-Octadecylsilsesquioxane, and Alumino n-Phenylsilsesquioxane were synthesized using the described template sol-gel approach. These ORMLAS materials are layered alumino-silicate structures having dodecyl, octadecyl and phenyl organic modifying groups, respectively in the interlayers, connected to the Si atom through Si-C bonds. X-ray diffraction patterns of the three ORMLAS materials are shown in Figures 5-7. Alumino-Dodecylsilsesquioxane displays the most ordered structure followed by Alumino-Octadecylsilsesquioxane and Alumino-Phenylsilsesquioxane respectively. Very sharp peaks reflecting a high degree of order in the layered structure are obtained for Alumino-Dodecylsilsesquioxane. A layer spacing of up to 3.9 nm is obtained from the XRD pattern. Four orders of the basal reflections are observed. The lack of non-integer orders of basal spacing also implies an ordered lamellar structure. The Alumino-Phenylsilsesquioxane does not show an ordered structure. This observation is consistent with our experience with the nature of ordering in ORMLAS materials.

A Transmission Electron Micrograph clearly showing the layers in Alumino-Dodecylsilsesquioxane powder is displayed in Figure 9. The powders were dried in air at ~75°C, were dispersed in ethanol and placed on Cu grid for placing

inside the microscope. The TEM picture was obtained at 120 kV, and at a magnification of 200K. The bar in the bottom right hand side represents 20 rim on the picture. Hence, an estimate of the layer spacings has easily been obtained. The layer spacing of (~ 4 nm) revealed in the micrograph matches that obtained from the  
5 XRD patterns (Fig. 5A).

The above-referenced ORMLAS synthetic methods have been improved. For example, it has been found that alumino - dodecylsilsesquioxane has consistently yielded the most well-ordered layered structure. Thus much standardization and  
10 streamlining effort has been applied to this organic modification.  $\text{AlCl}_3$  and Dodecyl triethoxysilane were used as sources for Al and Si respectively. Their electrostatic interactions were controlled by adjusting the pH using NaOH. Ethanol was used as the solvent. The synthesis process is simple and consistent, and yields layered structures reproducibly.

15 Accordingly, the present invention also features methods for modifying spacing between the inorganic silicate layers of ORMLAS which method includes adjusting the pH of a solution comprising the ORMLAS under conditions that enable achievement of the desired spacing. As discussed, preferred d-spacing can be  
20 determined by TEM or other suitable technique.

## Example 2 -Synthesis of ORMLAS with Lower Organic Content

### A. ORMLAS

25 It has been found that the ORMLAS materials that give the best dispersion in a polymer matrix are those prepared with long chain alkyls. It was found, however, that the glass transition temperature ( $T_g$ ) increased dramatically with increased clay loading. This will often be detrimental to heat distortion and may negate benefits obtained by good clay dispersion. Although not wishing to be bound by theory, one  
30 reason for this is likely due to plasticization caused, e.g., by the large amount of organic within these synthetic clays.



In order to lower the organic content within these clays, two synthetic methods were developed. Since large d-spacings were preferred, silane precursors with relatively long chain alkyl groups were used. But, some of these silanes were replaced with shorter chain alkyls as well as non-alkyl groups such as methyl.

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**Table 1. ORMLAS Materials with Lower Organic Content**

$C_{18} Si(OEt)_3$	$C_1 Si(OEt)_3$ or $Si(OEt)_4$
90	10
75	25
50	50
25	75

Assuming the standard XRD test suggests a significantly layered structure, the resulting nanocomposites will have a much lower extraneous organic content. This will alleviate the problem with the lowering of  $T_g$  observed for ORMLAS nanocomposites.

**B. ORMLAS Materials with Lower Organic Content**

10

Low organic content ORMLAS clays were synthesized by adding various amounts of a long chain silane along with a short chain silane. In each case, the long chain was dodecyl ( $C_{12}$ ) and the short chain was methyl ( $C_1$ ). The results of these syntheses are shown in Table 2, below, for methyl. The table includes the yields (measured and theoretical), the XRD peaks (001, 002, 003, along with the full width half maximum (FWHM), the mass loss from the TGA, and the elemental analyses. This data take to first determine if the layered phase was formed, how crystalline it is, and whether or not the short chain silane is incorporated within the structure.

20

It appears as if the layered phase is formed up to the inclusion of at least 50% of the methyl silane. The d-spacing decreases regularly with the increase of methyl content. This is consistent with a relaxation of the  $C_{12}$  chains with less organics holding the layers open. The amount of mass loss from the TGA, the consistent yield obtained, and the elemental analyses are consistent with the incorporation of methyl into the structure.

25

**Table 2. Lower organic C<sub>12</sub> ORMLAS Synthesis as a function of the Addition of Methyltriethoxysilane**

Mol% methyl dodecyl	Yield		XRD			TGA	EA Mas-%		
	Meas. (g)	Theo (g)	001/FWHM (Å) 2θ	002	003	(%loss)	C	H	C Theo
100%	1.75	2.0	39.4 / 0.40	19.6	13.2	61.07	59.7	9.90	57.4
10	1.64	1.89	37.7 / 0.384	18.9	12.6	59.09	53.5	9.73	55.5
20	1.53	1.76	37.1 / 0.422	18.4	12.5	58.53	50.9	9.38	53.4
30	1.45	1.64	36.6 / 0.512	18.4	12.3	57.40	50.0	9.21	50.9
40	1.26	1.52	36.1 / 0.636	18.4	12.5	56.34	48.5	9.06	48.1
50	1.13	1.39	36.2 / 0.781	18.4	None	53.11	45.7	8.70	44.8

5 Meas. = Measured  
Theo = Theoretical

Figure 12 is a table showing a list of alkyl and phenyl ORMLAS materials and d-spacings.

10

### Example 3 -Synthesis of Phosphonium Exchanged Clays

#### Phosphonium Clays

1. The phosphonium exchanged clays using tetraoctyl, dodecyltriphenyl, and tetra phenylphosphonium showed great promise due to their thermal stability. However in some instances there was minimal intercalation or exfoliation with Ultem during extrusion. Thermogravimetric analysis showed that they had very high thermal stability. The onset of exothermic mass loss for these materials occurred above 300°C and the peak of the exotherms appeared above the extrusion temperature for Ultem. This thermal stability is highly desirable making them usable for compounding with polyetherimide and other high temperature thermoplastics. Also, when these three phosphonium clays were extruded with Ultem, there were no signs indicative of burning or charring either by visual inspection, or by TEM.

2. Positive results for intercalating various polymers within the C<sub>16</sub> phosphonium clays were observed. It was thought to be helpful to use longer chain

phosphoniums. Preferred phosphoniums for use in this example were available commercially or were made *de novo*.

- 5  $C_{18}$  tributyl phosphonium bromide was prepared via direct reaction of equimolar amounts of octadecyl bromide (2.676g, 8.02 mmol) and tributylphosphine (1.624g, 8.02 mmol) in toluene (10 ml). The reaction was refluxed for 16 hours, after which the solvent was removed *in vacuo* leaving a crystalline solid. This was recrystallized in toluene / ether to a fine white powder.



- 10 To prepare the phosphonium exchanged montmorillonite, the phosphonium was exchanged with  $Na^+$  within natural clay.  $Na^+$  montmorillonite (20g) was sonicated with 1000 ml of deionized water in an ultrasound bath at  $80^\circ C$  for 1 hour. One and half equivalents of the as-synthesized  $C_{18}$  tributylphosphonium bromide (16.07g, 1.5 eq) dissolved in 20 ml ethanol was added resulting in a white precipitate.
- 15 This was stirred for 16 hours, then filtered and washed with 2000 ml  $H_2O$  and 1000 ml  $EtOH$ .

The resulting XRD pattern showed peaks corresponding to a d-spacing of 21.4 Å.

20

- The XRD results from the nanocomposite of the three previously prepared phosphonium clays indicate that there was incomplete or no exfoliation of the silicate layers. Therefore, new clays were prepared with phosphoniums having longer alkyl groups. These new clays were prepared by ion exchange of  $Na^+$  Montmorillonite
- 25 (100cc/100g) with hexadecyl (C16) triphenylphosphonium bromide and C16 tributylphosphonium bromide. This was accomplished via first an aqueous suspension of the clay in an ultrasound bath to break up the particles, then adding 2x excess of the phosphonium bromide, resulting in a white precipitate. After stirring for

one day, this solid was filtered, washed with water, and air-dried. The XRD results for these materials are shown in Table 3 below.

**Table 3. XRD Results for Phosphonium Exchanged Clays**

	<b>Phosphonium</b>	<b>d-spacing (Å)</b>
a	Tetraoctyl	22.3
b	Tetraphenyl	16.5
c	Dodecyl Triphenyl	16.5
d	C16 Triphenyl	34.4
e	C16 Tributyl	21.8

5

### 3. Lower Exchanged Phosphoniums

To help reduce or eliminate an undesired lowering of the glass transition temperature ( $T_g$ ), organic content of particular nanocomposites was reduced by lowering the amount initially used for the ion exchange of the natural clays. The method outlined above for ion exchange was followed, except lower amounts of the phosphonium bromide were used as shown in Table 4, below.

**Table 4. XRD Results for Low Exchange C<sub>16</sub> TributylPhosphonium Clays**

<b>Type of Phosphonium</b>	<b>Amount of Phosphonium added</b>	<b>d-spacing (Å)</b>
C <sub>18</sub> tributyl	1.5	21.40
C <sub>18</sub> tributyl	0.75	20.08
C <sub>18</sub> tributyl	0.5	17.14
C <sub>18</sub> tributyl	0.25	15.41
C <sub>16</sub> tributyl	1.5	21.08
C <sub>16</sub> tributyl	1.0	20.03
C <sub>16</sub> tributyl	0.75	19.54
C <sub>16</sub> tributyl	0.5	16.66

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As can be seen from Table 4, above, the d-spacing for the lower-exchanged phosphonium clays clearly decreases with lower phosphonium content. This is consistent for a clay with less organic pillaring the layers apart. Each of these materials was extruded with Ultem 1010, as shown elsewhere in this disclosure. All of them result in intercalated or exfoliated nanocomposites. That is, increased d-spacing was observed.

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